THE EFFECT OF STRESS ON THE CORROSION OF ALUMINIUM-MAGNESIUM ALLOYS

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CONTENTS.

CONTENTS:

INDEX OF TABLES AND FIGURES.

INDEX OF TABLES AND FIGURES.

INTRODUCTION.

INTRODUCTION.

Stress-corrosion may be regarded as the acceleration of the rate of corrosion of metals and alloys under the combined influence of static stress and corrosive environment. The term stress, when used in respect of stress-corrosion, almost invariably implies tensile stress since there are no reported observations of stress-corrosion failures resulting from corrosion under compressive stresses. Stress-corrosion cracking has been described as a specific case of the general phenomenon of stress-corrosion, the specific element being the limiting of the corrosive attack to a plane of microscopic dimensions or in fact subcrystalline dimensions. The plane of maximum cracking is persistently normal to the direction of highest tensile stress which may be residual or externally applied. In alloy rods stressed in torsion the plane of stress-corrosion cracking arises at an angle of 45° to the long axis or in other words perpendicular to the plane of maximum sheer (tensile) stress.

The principal factors involved in stress-corrosion cracking are stress, environment, composition, internal structure and time. Almost all structural metal systems are susceptible to

stress-corrosion. Brass, steels, stainless steels, zinc alloys, aluminium alloys, magnesium alloys, lead and nickel alloys have all been shown to be affected in the proper environment and indeed it has been stated that there exist corrosive environments which would cause stress-corrosion cracking of any known alloy system.

Stress-corrosion cracks may be either intergranular or transgranular in character depending on the nature of the alloy system and the corrosive environment. α-Brass in ammoniacal atmospheres, aluminium alloys in chloride solutions, and mild steel in nitrate solutions exhibit predominantly intergranular cracks while stainless-steels in acid chloride solutions, β-brasses and magnesium alloys, almost invariably crack in a transgranular fashion, although magnesium alloys possess the enigmatic property of cracking intergranularly in alkaline corrosive solutions.

The chemical conditions which produce cracking in the presence of stress appear to be specific to each system although they have in common the requirement that corrosive environments which are generally more conducive to stress-corrosion cracking are those which produce relatively mild surface

corrosion but highly localised attack. Along with environments already mentioned for brasses etc. there may be included aqueous HCN in the case of mild steel, moist H_2S for certain stainless steels and caustic soda for nickel.

The time required for complete stress-corrosion failure may vary from several minutes to months or more depending on the degree of stress and the corrosive environment. It is worth noting that while stress-corrosion failures in susceptible alloys can be produced at will under laboratory conditions very few service failures have been reported. In view of the widespread use of potentially susceptible alloys it is clear that the low incidence of failures is due mainly to the early recognition of the phenomenon of stress-corrosion, the rapid realisation of the critical part played by stress and the subsequent industrial efforts to reduce susceptibility, notably by the stress relieving of fabricated structures.

Various theories of stress-corrosion have been proposed and, while agreement has been reached concerning the initial stages of the reaction, disagreement exists as to the true functions of stress and corrosive environment subsequent to the initiation of the attack.

It is generally believed, however, that the main mechanism involved is electrochemical in character. Current theories and the various factors contributing to stress-corrosion cracking in susceptible alloy systems are discussed more fully in a later section, but with respect to aluminium/magnesium alloys with which this thesis is solely concerned it is sufficient to state at this stage that it is generally recognised that when these alloys are in a condition seriously susceptible to stress-corrosion there exist at the grain boundaries continuous films of the β-phase Al_3Mg_2(7, 8, 9.) This structural change results from heat treatment or ageing which is a function of time and temperature. Plastic deformation before thermal treatment or ageing results in a higher degree of grain boundary precipitation((9) & Fig. 46d). It has been shown (85) that there is a difference in potential between the grain body and the β-precipitate which is the anodic phase.

The object of this research was to extend the work carried out by E.L. Jones in 1954 (2, 3.) on the quantitative measurement of the stress-corrosion susceptibility of Al-5%Mg and Al-7%Mg to include the 3½%Mg and 2½%Mg alloys. Later it was found desirable to determine and compare the susceptibilities

of the latter alloys by the method of intermittent spraying and in general to compare the two methods of corrosion testing. The work was further extended to include a section on the effect of varying cross-section area on the stress-corrosion susceptibility of the 7%Mg alloy. This alloy was chosen because its test results tended to be more reproducible and its times-to-failure when corroded under applied stresses were shorter. The work was carried out on rods of varying British Standard Wire Gauges prepared from a single billet of the alloy. The whole of the material was commercially annealed at the same time and laboratory treatment prior to testing was uniform for each test-piece.

The method of evaluating stress-corrosion susceptibility is that described by E.L. Jones in the Journal of Applied Chemistry in 1954. Briefly the method determines the percentage of the ultimate tensile strength at failure which is due to stress-corrosion. This is calculated from the plots of (a) % Loss of U.T.S. vs. Time for the unstressed alloy and (b) % Loss of U.T.S. at failure (i.e. 100- applied stress as % U.T.S.) against the time to failure for the stressed material.

Terms are defined as follows:-

S_s^c = % Loss of U.T.S. at failure when stressed under static tensile stress. ...(1)

S_u^c = % Loss of U.T.S. of the unstressed specimen exposed for the time to failure of the stressed specimen. ...(2)

S_l^c = % Loss of U.T.S. of a specimen stressed to the same stress as (1) for the time to failure of (1) but not exposed to the corrosive environment.

$$\text{and } f_s^c = S_s^c - (S_u^c + S_l^c)$$

where f_s^c is the percentage of the loss of ultimate tensile strength which is due to stress-corrosion at failure.

In the work described in this report the value of S_l^c was consistently zero and was omitted from calculations the equation reducing to:-

$$f_s^c = S_s^c - S_u^c .$$

It can be seen that, ideally, maximum susceptibility to stress-corrosion implies that loss of strength at failure is entirely due to stress-corrosion. i.e. S_u^c remains at zero either because the corrosive environment is inert in the absence of stress or that

the time to failure is so short that it lies within an unstressed corrosion induction period or has progressed so little that its value is negligible. In this case $f_s^c(\text{Max.}) = S_s^c$ = (100- Applied stress as % U.T.S.). In Fig. 4 the line 100/100 satisfies this equation and represents the maximum % loss of U.T.S. due to stress-corrosion which is theoretically possible under any applied stress. Since for an alloy having no stress-corrosion susceptibility f_s^c is zero for all applied stresses the curve of f_s^c vs. applied stress (% U.T.S.) must lie within the area 100/0/100. The stress-corrosion susceptibility is then the area enclosed by the experimental curve expressed as a percentage of the area 100/0/100.

The results and conclusions shown should be interpreted not with respect to the commercial alloys as used under service conditions but in terms of alloys deliberately rendered highly susceptible to stress-corrosion and corroded under specific and carefully controlled conditions in a specific environment i.e. intermittent immersion in 3% aqueous sodium chloride.

INTRODUCTION (Continued.)

THEORETICAL ASPECTS OF STRESS-CORROSION.

The effect of stress on the internal structure of alloys.

In order to evaluate the effect of stress on the corrosion of alloy systems the effect of stress alone on the internal structure and physical characteristics of the alloys should be understood. This is particularly true when accelerated tests are used in conjunction with alloys of the type discussed in this thesis, since these have been deliberately overstrained in order to render them highly susceptible to stress-corrosion.

Plastic deformation resulting from the application of stress in excess of the elastic limit causes changes in the internal structure of alloys such as slip, twinning and disorientation, and fragmentation of grains into disorganised mosaics of crystallites. The extent to which any of these processes occur is dependent on the amount of deformation, the strain rate and the temperature of straining. Strain may also result in phase transformations and cause acceleration of solid state precipitation reactions, e.g. the precipitation of Al_3Mg_2 from aluminium-magnesium alloys (11) and the transformation of austenite to martensite in certain stainless steels. Characteristic changes

in physical properties such as resistivity (12) and magnetic properties also result from plastic deformation. Slip occurs by the gliding of one layer of atoms over a neighbouring layer although only about every thousandth layer moves in this way. Under a given load grains of different orientation take up different degrees of stress even within the elastic range. When gliding begins this stress difference increases and some grains with favourable orientation yield under a small load while others need higher stresses to achieve the critical sheer value necessary for slip. The variation in stress from grain to grain may be very high. This has been demonstrated elegantly by Orowan (13) who made use of the photoelastic properties of silver chloride to show the different degrees of stress between and within the grains, and by Boas and Hargreaves (14) who measured hardness and elongation at numerous points in large grained aluminium specimens. This heterogeneous deformation, with the associated highly localised areas of distortion, results in the production of residual stresses which may be of such magnitude that the application of even very small external stresses may be sufficient to cause cracking.

The Effect of Stress on Electrode Potentials.

Plastic deformation of a metal or alloy increases its internal energy. This is manifested by an increase in its heat of solution and by a negative shift in its electrode potential, i.e. it becomes more anodic. This is to be expected from the relationship:-

$$\Delta F = -nfE$$

where F is the change in free energy of the system, f is Faraday's constant, n is the number of electrons involved and E is the electrode potential. By determining the difference between the work done and the heat evolved during deformation, the energy stored in twisted iron during cold work has been measured. (15) The order of magnitude of the increase of internal energy is about 1 cal/g. indicating a change of potential of the order of millivolts. Plastic deformation is, however, a non-homogeneous phenomenon and the change in energy may be highly localised in which case a much higher order of local potential change may exist. In the case of high purity aluminium it has been shown (16) that cold working renders the potential in 3% NaCl about 50 mv. more anodic than the unworked metal and Bosshard (18) has observed that after 7 days corrosion, 93% cold worked

aluminium was more anodic by as much as 700 mv. than 50% cold worked aluminium. Work carried out on the corrosion fatigue of mild steel has shown that stresses within the plastic range render the potential of the metal more anodic irrespective of film effects. Within the elastic range, however, the effect of stress on the potential of mild steel not covered by a protective film appears to be negligible.(17)

Possible chemical effects arising from such potential changes are to be found in increasing rates of solution in acids. For example it has been shown that cold work greatly accelerates the action of hydrochloric acid on aluminium and magnesium (19) and that the rate of attack of dilute sulphuric acid on iron is greatly increased after straining.(20). With respect to aluminium and magnesium alloys perhaps the most interesting of such effects is the observation by Beerwald and Groeber (21) that the hydrogen evolved from an aged aluminium-magnesium alloy by the action of hydrochloric acid is more than doubled if the alloy is plastically strained before ageing.

Age-hardening.

The phenomenon of age-hardening which was discovered by Wilm in 1911 (22) in alloys of aluminium

and copper results in characteristic changes in various physical properties of the alloys concerned. Chief among these are hardness, tensile strength, density, electrical resistivity, specific heat, microstructure and lattice parameter. Various theories have been proposed to account for age-hardening (23,24,25,26,) but Gayler considers that in the case of aluminium-copper alloys hardening is due to strains set up as the result of segregation of copper atoms which form platelets on the [100] planes followed by the precipitation of copper rich aggregates and the formation of crystallites of new solid solution. (27) With aluminium-magnesium alloys in which the magnesium content is greater than the solid solubility at ordinary temperatures, i.e. 1.9%, (30,31,32,) the precipitate consists of the β-phase Al_3Mg_2. It is of interest to note here that it has been shown that the first formed β-phase precipitate of aluminium-magnesium alloys is unstable and, as ageing proceeds, is transformed into an equilibrium β-phase.(28)
Evans suggests that random distributions of atoms in the quenched solid solution tend to redistribute themselves to produce an ordered condition and consequently the work required for deformation will be increased, i.e.

the alloy will become harder. Cold work accelerates age-hardening or, in other words, the application of an external stress during the process of ageing increases the rate of increase of submicroscopic and microscopic internal stresses generated during the ageing process. (29). Gayler's statement that the submicroscopic and microscopic internal stresses associated with ageing may affect the direction of development of stress-corrosion cracks and accelerate their formation under applied external stress is considered to be significant. The fact that these stresses are associated with the formation of solute rich aggregates in crystallographic planes may explain the incidence of transgranular cracking in magnesium alloys and certain stainless steels.

Grain Boundary Phenomena.

Metals do not normally exist in the form of single crystals but as polycrystalline aggregates in which the bulk of the metal is made up of a large number of interlocking crystals or grains. Each grain is connected at all points on its surface to its neighbours by a grain boundary which is generally of irregular shape and bears no relationship to the

internal symmetry of the crystal. Grain boundaries are in themselves regions of stress resulting from the mismatching of adjacent grains of different orientation and can be responsible for intergranular corrosion. High purity aluminium containing grains of random orientation is corroded by hydrochloric acid but when the relative orientations are nearly identical no corrosion occurs. (33). E.H. Dix has reported a case of aluminium alloy tubes which, due to residual stress and corrosive environment, developed only longitudinal cracks although the longitudinal residual stresses were twice as high as the transverse stresses present. (34.) He suggests that the explanation lies in the more direct longitudinal path offered by the axial elongation of the grains. A similar observation has been reported by Davis (35) who draws attention to the industrial practice of fabricating stainless steel bellows-type expansion joints so that the grain of the metal, i.e. the direction of rolling of the sheet, is parallel to the axis of the joint. The only failures which he experienced were in expansion joints which had been subjected to a shearing stress due to misalignment. Variations in boundary energy with orientation of grains have been observed in silicon ferrite (36) and in tin (37) and studies of thermally etched silver have shown

that the boundary energy varies with the angle between the crystal boundaries. (38)

The existence of mosaic subgrains in high purity aluminium has been demonstrated by LaCombe and others. (39,40,41,42.) These subgrain boundaries tend to become regions where dissolved elements concentrate preferentially and probably have some bearing on the phenomenon of transgranular cracking. It has been shown that in the case of coarse-grained aluminium the breakdown of grains into subgrains is more marked at the grain boundaries (43) and that the less ductile magnesium forms crystallite debris at the boundaries when grains break down into subgrain cells. (44) Edmunds (45) has observed that a single crystal of α-brass failed rapidly under an applied tensile stress of 10,000 p.s.i. in an atmosphere of ammonia and concludes that grain boundaries do not appear to be necessary for stress-corrosion cracking to take place. This suggests that the condition causing selective corrosion at grain boundaries must also exist within the grain at regions such as slip planes or mosaic subgrain boundaries. These regions of lattice imperfection may be expected to possess a higher free energy which would manifest itself in higher solution potential and greater stress-corrosion susceptibility.

Dix and Brown (46) measured the potential difference between grain bodies and boundaries and were able to show that the grain boundaries of quenched high purity aluminium were anodic to the grain bodies but were cathodic if the metal, instead of being quenched, were slowly cooled; the grain boundaries of large grained annealed 70-30 brass were anodic in ammonia solutions. Dix was also able to show that when an aluminium-4%-copper alloy was quench-aged so that solute depletion took place at the grain boundaries as a result of boundary precipitation of $CuAl_2$ the depleted zones were anodic to the grain bodies. Furthermore the curve of potential difference against ageing time passed through a maximum after 9 hours at 190°C and dropped to zero after 32 hours. Linear overstraining to the extent of 5% before ageing produced a similar maximum but occurring after 4 hours with the curve dropping to zero after 16 hours. It should be noted that both the depleted zone and the grain body are anodic to the boundary precipitate of $CuAl_2$ whereas in the case of strain-aged aluminium-10%-magnesium the boundary precipitate of Al_3Mg_2 is more anodic than either the grain body or the depleted boundary zone.

Environment.

The chemical condition which, in the presence of internal or applied tensile stress, produces cracking of an alloy, is generally regarded as being individual to the alloy system. This point of view receives substantial support from the apparently selective nature of corrodents reported extensively in the literature of stress-corrosion. For example aluminium base alloys crack in NaCl solutions, gold-copper-silver alloys in $FeCl_3$ solutions (47), copper base alloys in ammonia and ammines, (48) 18-8 stainless steels in $MgCl_2$ (49) and so on. Doubts have been expressed about the emphasis placed on such a generalisation (50) and Keating has pointed out (51) that the present awareness of stress-corrosion corrodents is largely due to the incidence of industrial failures, usually in a specific environment, rather than to the results of studies of large numbers of corrodents. Some grounds for such doubts are provided by the realisation that mild steels crack in such diverse media as $NaOH-Na_2SiO_3$, $Ca(NO_3)$, NH_4NO_3 and aqueous HCN while 18-8 stainless steels have been shown to crack in the presence of moist H_2S as well as in $MgCl_2$. (52). Madden (53) has observed the cracking of magnesium base alloys in distilled water as

well as in the classic NaCl solutions and 18-8 type stainless steels have been reported failing in steam condensate containing as little as 18 p.p.m. chloride.(35) On one point however there is general agreement and that is that the corrosive medium must be one which produces an effect between the extremes of general corrosion and passivity.

With respect to aluminium-magnesium alloys the most satisfactory corrodent in laboratory use for accelerated tests is 3-3½% NaCl. As suggested previously, the use of NaCl probably arose from attempts to reproduce naturally occurring corrodents e.g. sea-water and not from a study of possible alternatives. It is to be expected that the majority of failures in the field would be caused by the most active (from the point of view of stress-corrosion) and, at the same time, the most wide spread corrodents and NaCl appears to qualify in both respects. The stress-corrosion life of Al-7%Mg decreases rapidly as the NaCl concentration increases from 1.5 to 3.0% and thereafter, up to 25%, remains comparatively unchanged as shown in Fig. 46e.(54)

The pH of the corrosive solution has a critical effect on the general pattern of stress-corrosion. The time to stress-corrosion cracking of susceptible Al-7%Mg in 3% NaCl decreases with increase in acidity down to

pH 1 although in strongly acid solutions there is a slight tendency towards increased time to cracking due to interference by overall intercrystalline attack. With solutions of pH 10 or greater stress-corrosion cracking is inhibited. (55,56). Magnesium base alloys are affected similarly in chromated 3.5% NaCl at pHs in excess of 12. (57).

Perryman and Hadden have reported that Al-7%Mg rendered susceptible to stress-corrosion and stressed in 3% NaCl does not crack in the absence of oxygen. Failure occurs rapidly however in aerated solutions and specimens which remain free from cracking for long periods in deaerated solutions fail rapidly on admission of air. (54). There are indications that failure may be a little slower in corrosive solutions saturated with oxygen than in those saturated with air. The presence of carbon dioxide has been found to be non-essential for stress-corrosion cracking. (57).

Oxygen is also essential for the ammonia stress-cracking of brass (59) and it has been suggested that, with respect to wrought β-brasses with and without the addition of aluminium, oxygen may play some part in controlling the direction which the crack takes and the rapidity with which cracking takes place. (60).

The Nature of Stress-corrosion.

Stress-corrosion has been defined jointly by Sutton, Lidiard, Chalmers and Champion as the greater deterioration in mechanical properties of a material through the simultaneous action of static stress and exposure to corrosive environment than would occur by the separate but additive action of those agencies. (61) This definition has been mildly criticised on the grounds that it does not distinguish between the possible acceleration of general corrosion which would normally take place in the unstressed condition and the initiation of another type of attack such as stress-corrosion cracking which is never present in the absence of tensile stress whether residual or applied. (62) For example Robertson has observed that in non-susceptible high strength aluminium alloys a pitting type of corrosion occurs in salt solution and that the rate of corrosion is increased by the application of tensile stress. (63) Stress-corrosion cracking implies the initiation and propagation of cracks, whether intergranular or transgranular, by the action of tensile stress and a corrosive environment and, while there is no evidence to suggest that in the absence of stress the corrosive environment alone can give rise to cracking, unless an intergranular ditch can be regarded

as a crack, pure stress cracks have been produced in susceptible Al-7%Mg by Gilbert and Hadden. (64) Champion perhaps more than anyone has repeatedly insisted that researchers in this field should be quite clear on what is meant by the term stress-corrosion and Dix has deprecated the loose manner in which the term is sometimes used. He suggests that stress-corrosion cracking may be considered as a specific phase of the more general subject of high constant stresses in accelerating the rate of corrosion of metal products. Dix lays down two criteria for the acceleration of corrosion by constant stress. (66) These are:- (a) there must exist in the alloy a susceptibility to selective corrosion along one or more continuous paths, e.g. at grain boundaries-(b) there must exist a condition of high stress acting in a direction tending to pull the metal apart along these paths. Selective corrosion resulting from the presence of anodic zones developing from composition differences or strain gradients or from local breakdown of protective films produces pits or trenches. Regions of stress concentration are thus formed and under the combined action of stress and corrosion these cracks are propagated.

It is generally recognised that when aluminium-

magnesium alloys are in a susceptible condition with respect to stress-corrosion an almost continuous precipitate of the β-phase Al_3Mg_2 exists at the grain boundaries. (67,68,69.) The β-phase is anodic to the solid solution in chloride solutions and is corroded preferentially. Vosskuhler has shown however that the β-phase is not attacked preferentially by 5% NaOH but that above an alloying percentage of 5% it is attacked almost exclusively by 1% HCl. (70) (See also Figs. 46a, 46b) Since the stress-corrosion behaviour of aluminium-magnesium alloys is so closely associated with grain boundary Beta precipitation it appears reasonably certain that the mechanism of stress-corrosion must involve this precipitated phase. Aluminium-magnesium alloys show good resistance to acid attack if the grain boundary precipitate is characterised by a discontinuous "necklace" structure. (71,72) This structure is illustrated by Mockel (73) and is similar to a condition discussed by Perryman and Hadden (74) who, however, found that a specimen exhibiting a "necklace" Beta structure failed faster by a factor of 8 when stress-corroded in NaCl solution than a comparable specimen showing a much more continuous Beta network. It is perhaps worth noting in view of this apparent contradiction that prolonged heat treatment has

been shown to minimise the susceptibility to intergranular corrosion of austenitic stainless steels. The explanation here appears to lie in the transformation of chromium carbide from a dendritic to a geometric form and does not involve the solute depleted zone which is generally considered to be the anodic path of intergranular attack. (75)

Theories of Stress-corrosion Cracking.

Environments which are most conducive to stress-corrosion cracking are those which produce relatively little surface corrosion but highly localised attack. It is in fact true to say that the majority of laboratory induced failures by stress-corrosion cracking show little visual evidence of general corrosion. Localised corrosion in an alloy may result from composition differences, the local breakdown of protective films or critical differences in the orientation between grains. There is more or less agreement on the initial mechanism of attack but as Dix has pointed out (66) there must also exist a susceptibility to selective corrosion along continuous paths for stress-corrosion to take place. With his associates he is of the opinion that stress-corrosion

is electrochemical in character, the localised path being the anode and the surrounding metal the cathode. The anodic path may be a precipitated phase at the grain boundary e.g. Al_3Mg_2 in the case of aluminium-magnesium alloys or a solute depleted zone adjacent to the grain boundary such as the new boundary solid solution resulting from the precipitation of $CuAl_2$ in duralumin type alloys or chromium carbide in certain stainless steels. (76)

They suggest that stress concentration at the base of trenches developed by localised corrosion disrupts the metal by mechanical action and exposes fresh unfilmed material to the corrosive environment. Since the freshly exposed metal is more anodic acceleration of corrosion is brought about by an increase in the current flow from the base of the crack to the unaffected surface. The electrochemical theory explains the non-susceptibility to stress-corrosion cracking of certain aluminium alloys after prolonged ageing at elevated temperatures on the grounds that precipitation in the grain bodies results in a loss in potential difference between the grain bodies and the boundary zones. The fact that cathodic protection can prevent stress-corrosion cracking in some magnesium (76) and aluminium-magnesium (4) alloys has been offered in

support of an electrochemical theory and the phenomenon at least indicates that electrochemical corrosion is an essential partner in what may be a chemical-mechanical cycle. In considering the advance of an actively propagating crack Evans (78) visualises hold-up occurring due to obstruction by chemically strong and/or mechanically strong barriers. The chemically strong barriers will be ruptured by stress concentration and those mechanically strong will be accounted for by chemical action. Mechanical hold-up is indicated by jerks in corrosion extension curves (4) and chemical hold-up by jerks in corrosion potential curves. (79)

Keating is of the opinion (78) that crack initiation results from corrosion pits which are opened up by stress concentration and propagate solely by the mechanical action of stress until arrested by an obstacle such as a non-metallic inclusion or an unfavourably oriented boundary either of which reduce the stress concentration to an ineffective level. Corrodent then slowly diffuses to the crack tip and by its action produces fresh points of stress concentration and the subsequent repetition of mechanical propagation. The theory has been criticised by Allen (80) on the grounds that stress-corrosion cracking would be encountered wherever the corrosion conditions were such

as to cause a pitting type of attack and also that it fails to explain the apparent strong association between a specific corrodent and a particular alloy system.

Champion (81) favours a system of stress concentration at the base of a crack, increasing with depth and change of radius of curvature until relieved by plastic deformation. The yielding of the crack tip causes film failure and corrosion takes place by an electrochemical mechanism. He suggests that the main effect of stress in stress-corrosion comes just before failure and is closely associated with film failure. This view is supported by Edeleanu's observation that the overall time to failure of a susceptible Al-7%Mg alloy was unaffected if stress were omitted during the first 80% of the stress-corrosion life of the specimen.

Gilbert and Hadden have proposed a theory (56) concerned particularly with the mechanism of stress-corrosion of Al-7%Mg in which they visualise a three stage cycle as follows:- (a) slow intercrystalline corrosion, (b) mechanical disruption caused by stress concentration, and (c) rapid intercrystalline attack. The theory is closely similar to the general theory of Dix et al. (76)

The theories which have been outlined above are based on the pre-existence of a metallurgical condition which renders the metal highly susceptible to corrosive attack along highly localised paths and for this reason have been criticised on the grounds that they do not adequately explain the incidence of stress-corrosion cracking in homogeneous alloys such as α-brass and certain stainless steels which show little susceptibility to corrosion in the absence of stress. In an attempt to overcome these objections Waber (82,83) has extended the electrochemical theory to include a strain accelerated decomposition of a meta-stable phase. As a result of stress concentration at the tip of a crack, the meta-stable phase is decomposed faster than the bulk of the metal. One of the decomposition products is anodic to the parent matrix and the crack proceeds by forming new anodic material ahead of its path. The theory assumes that strain will accelerate the decomposition reactions of apparently homegeneous phases and states that the reaction may result in a single reaction product e.g. the conversion of austenite to martensite in certain stainless steels or have two reaction products such as a precipitated phase and the resulting adjacent depleted solid solution. In support

of the theory there is no doubt that cold work increases the speed of ageing processes (84) in metal systems in which stress-corrosion susceptibility depends on precipitation reactions.

EXPERIMENTAL Part I.

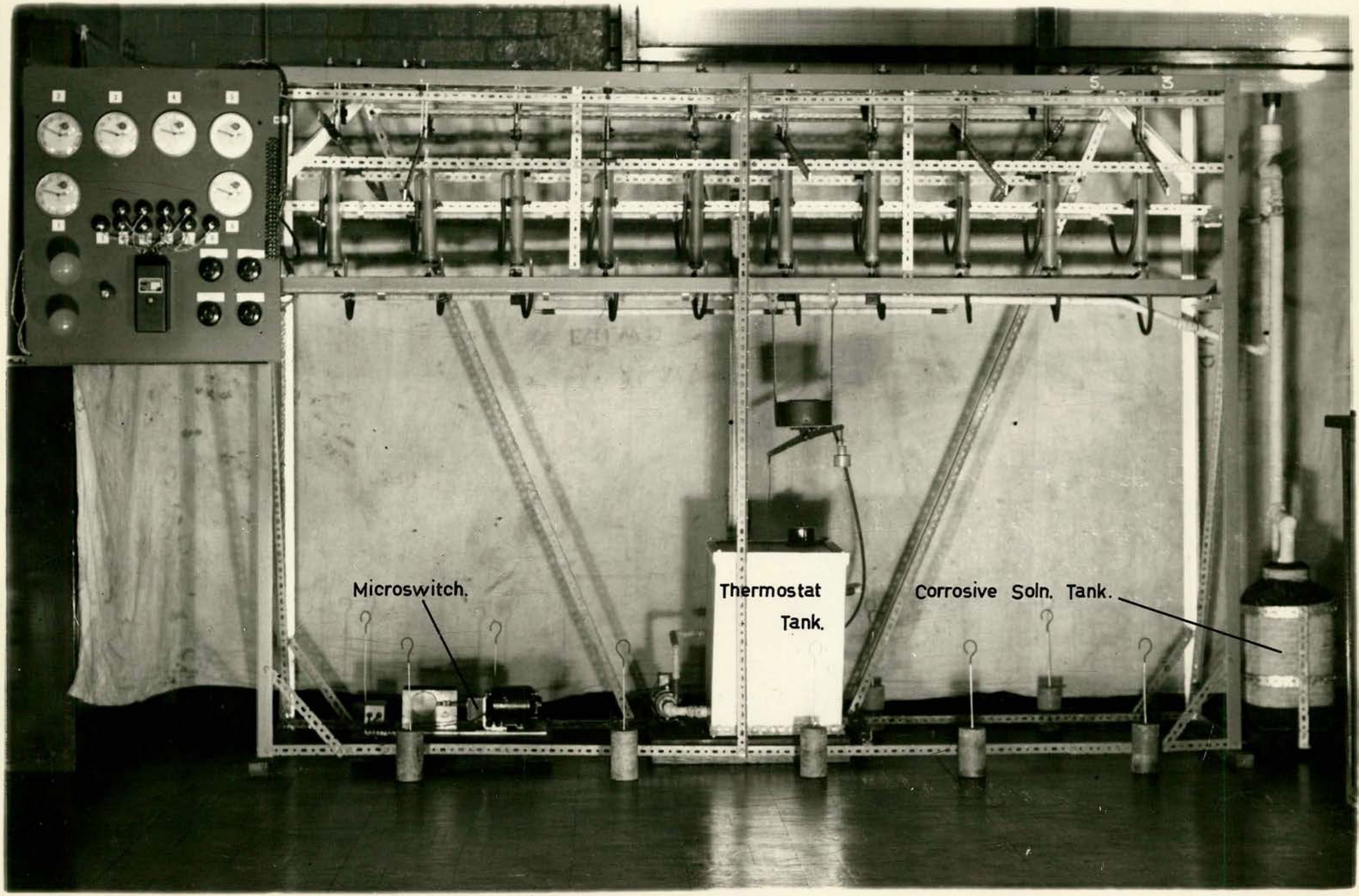
EXPERIMENTAL Part I.

THE STRESS-CORROSION SUSCEPTIBILITY OF Al-3½%Mg AND Al-2½%Mg.

Materials and preparation of test-pieces

Aluminium-2½% and 3½%-Magnesium (nominal) alloys, in the form of 16 S.W.G. wires, commercially annealed, were cut into 14 inch lengths and each length overstrained 10% in tension. (1,2) (Fig. 46f.) The test lengths were then cleansed and degreased by immersion for 2 minutes in 10% nitric acid followed by washing for 5 minutes in cold running water. After drying and lightly rubbing with filter-paper the wires were aged in a hot-air oven at 125°C for 24 hours. The choice of this ageing time and temperature was based on the results of work carried out by Perryman and Hadden (1) and reproduced in part in Fig. 46d. The final stage in the preparation of the test-pieces consisted of protecting the ends of each wire with polymethacrylic resin so that only a 7 inch length remained exposed in the middle of each specimen. (2)

The chemical analyses of the alloys used are shown in Table 1. Average mechanical properties were determined on random samples of the finished test-pieces and are shown in Table 2.



INTERMITTENT IMMERSION APPARATUS.

Fig. 1.

Corrosive Solution.

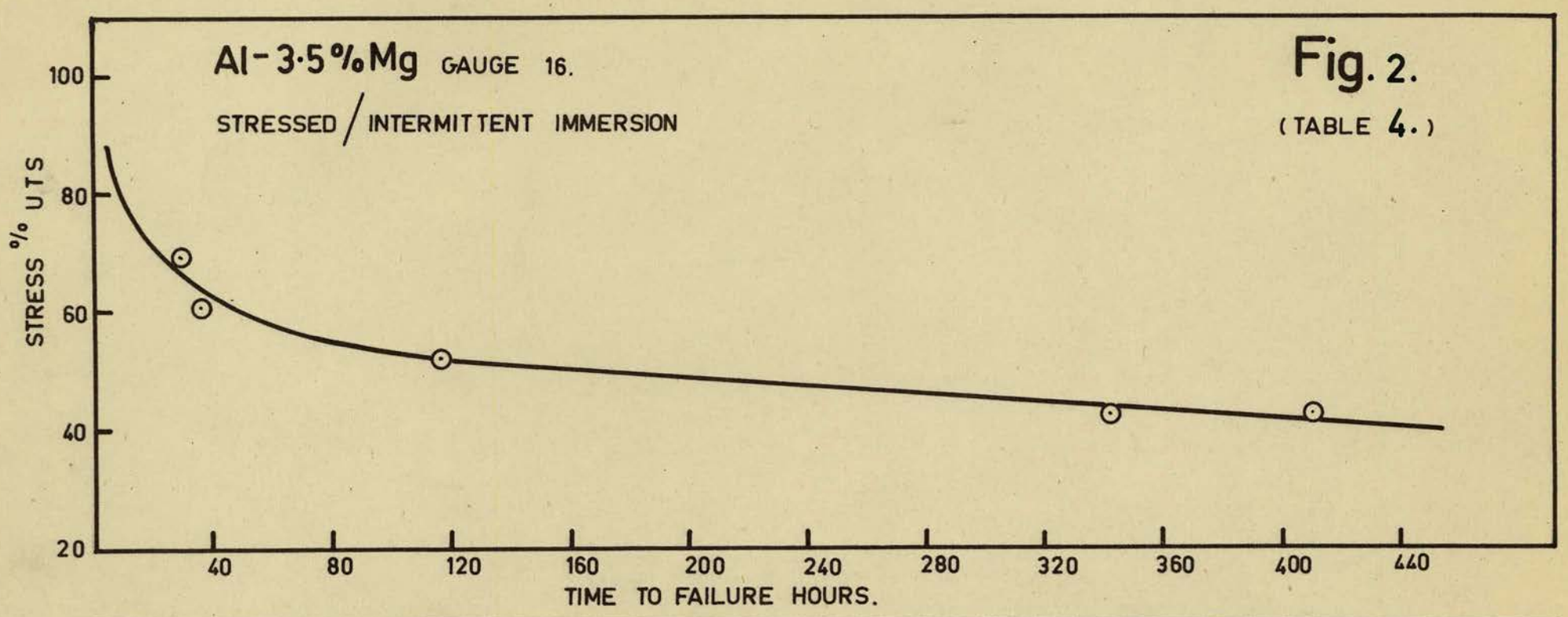
The corrosive solution consisted of 3% w/v aqueous sodium chloride buffered to pH 6 by the addition of 1.6% sodium acetate and 0.06% acetic acid. (1,2) Fig. 46e. In the preparation of the solution analytical quality reagents and distilled water (cast-iron/glass still) were used throughout.

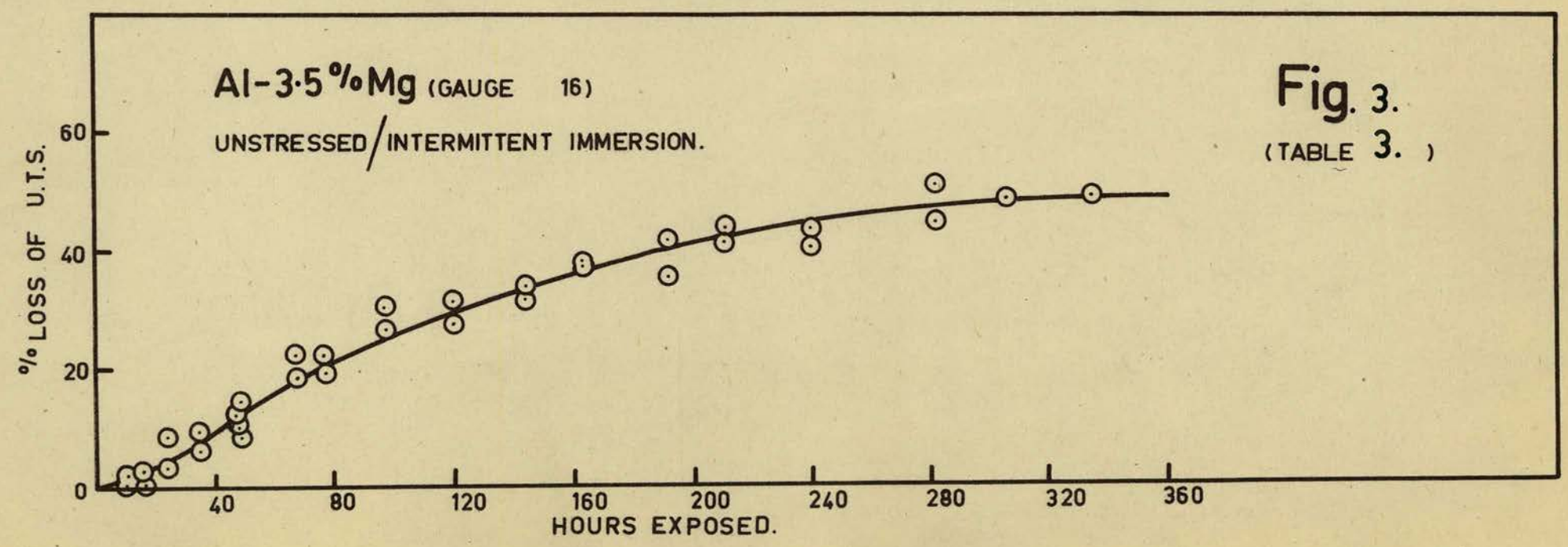
Apparatus and Method of Testing.

The apparatus used was similar to that described by Jones in a report on work carried out on Al-5% and 7%-Mg alloys and consisted chiefly of ten water-jacketed corrosion tubes mounted on a metal frame. Fig. 1. Corrosive solution was pumped intermittently to an overhead constant level overflow reservoir from which it gravitated to the corrosive solution tubes in such a way that all the tubes filled from the bottom at the same time, to the same level, at the same rate. Water from a tank maintained at 27°C circulated in the tube jackets and, in conjunction with asbestos and felt lagging on the manifolds and corrosive solution reservoir, maintained the temperature of the corrosive solution at 25°C$\mp\frac{1}{2}$°. The corrosive

solution pump was controlled by a microswitch activated by a mechanical cam which was rotated through a gear train by an induction wound constant speed motor. The cam rotated once in 12 minutes and was so shaped that the microswitch was open for 2 minutes and closed for 2 minutes. The wires were anchored underneath a $3\frac{1}{2}$ x $2\frac{1}{2}$ inch channel iron by means of steel-block vises and stressed by steel-yards having a 10:1 mechanical advantage. At failure the dropping of a steel-yard opened an overhead time switch and stopped an electric clock which was recording the stress-corrosion life of the specimen. The control panel incorporated a switch board by means of which any one of 6 clocks could be allocated duty at any chosen tube.

Test specimens were subjected to intermittent immersion in the corrosive solution both in the stressed and unstressed condition. The cycle of immersion was such that each test-piece was submerged for 2 minutes and then exposed to air in the wet condition for 2 minutes. The chloride content of the corrosive solution was determined daily and water losses made up with distilled water when necessary.

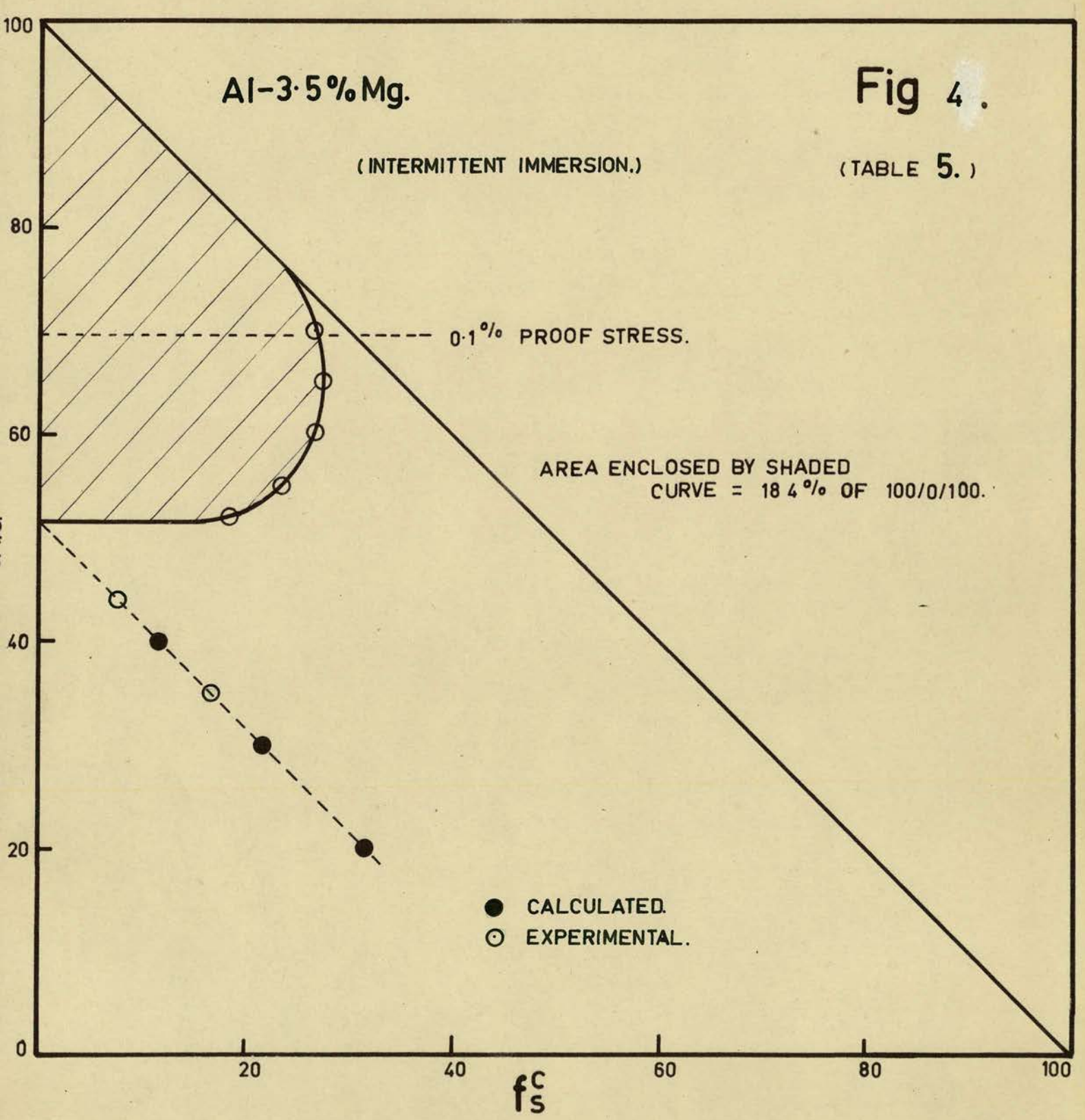

Al-3·5%Mg GAUGE 16.
STRESSED / INTERMITTENT IMMERSION
Fig. 2.
(TABLE 4.)
STRESS % UTS
100
80
60
40
20
40
80
120
160
200
240
280
320
360
400
440
TIME TO FAILURE HOURS.


Al-3·5%Mg (GAUGE 16)
UNSTRESSED / INTERMITTENT IMMERSION.
Fig. 3.
(TABLE 3.)
% LOSS OF U.T.S.
60
40
20
0
40
80
120
160
200
240
280
320
360
HOURS EXPOSED.

Experimental Results.

(a) Aluminium-3½%-Magnesium.

The unstressed corrosion-time curve is shown in Fig. 3 and Table 3. The curve exhibits a short induction period of approximately 20 hours and a maximum loss of ultimate tensile strength at 280 hours. A large number of experimental points were used in the construction of the curve since it was expected that the alloy represented a border-line case with respect to stress-corrosion susceptibility and a wider range than usual of experimental variation was therefore expected. In order to show that the flattening of this curve was not due to the deposition of suspended hydroxide on the surface of the test-piece a further series of tests was carried out in which the specimens were cleaned every 24 hours. Film was removed by immersing the wires for about 2 seconds in 10% nitric acid and then washing thoroughly with cold running water. The wires were wiped with filter paper before being returned to the corrosion tubes. Fig. 20, Table 19 shows that film removal had very little effect on the characteristics of the unstressed corrosion-time curve.


Al-3·5% Mg.
Fig 4.
(INTERMITTENT IMMERSION.)
(TABLE 5.)
0·1% PROOF STRESS.
AREA ENCLOSED BY SHADED CURVE = 18·4% OF 100/0/100.
CALCULATED.
EXPERIMENTAL.
100
80
60
40
20
0
20
40
60
80
100
f_s^c

Specimens corroded under applied stresses of between 43.5% and 69.6% of the ultimate tensile strength (U.T.S.) showed a fairly wide spread of times to failure and the means of larger than usual numbers of determinations were used to construct the corrosion-time curve. (Fig. 2, Table 4). It can be seen that at stresses below 52% of the U.T.S. the curve becomes asymptotic to a sloping line which intersects the time axis.

The stress-corrosion susceptibility of the alloy as assessed by the method of Jones (3) and shown in Fig. 4 and Table 5 was 18.4%. Times to failure for applied stresses below about 50% of the U.T.S. fall within the flat region of the unstressed curve and hence S_u^c for lower stresses remains constant at 49%. The plot of stress vs. f_s^c becomes, therefore, a straight line intersecting the stress axis.

(b) Aluminium-2½%-Magnesium.

The unstressed corrosion-time curve (Fig. 5, Table 6) shows a prolonged induction period of approximately 150 hours and rises to a maximum loss of U.T.S. at 260 hours thereafter becoming asymptotic

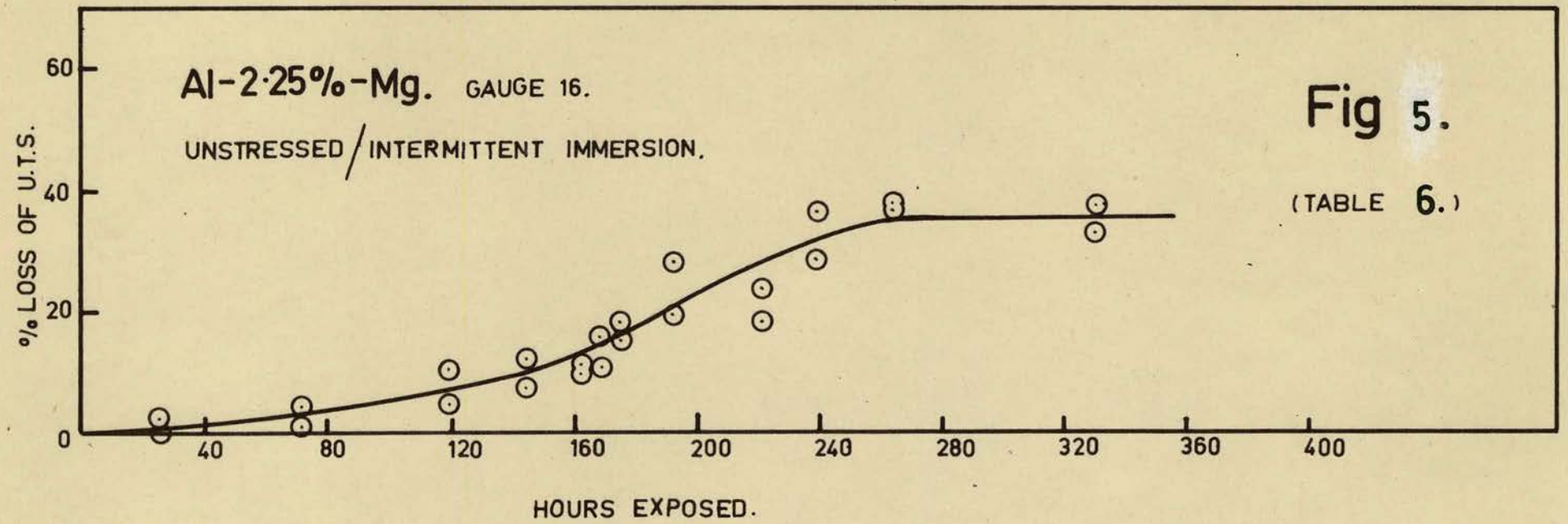


Fig 5.

(TABLE 6.)

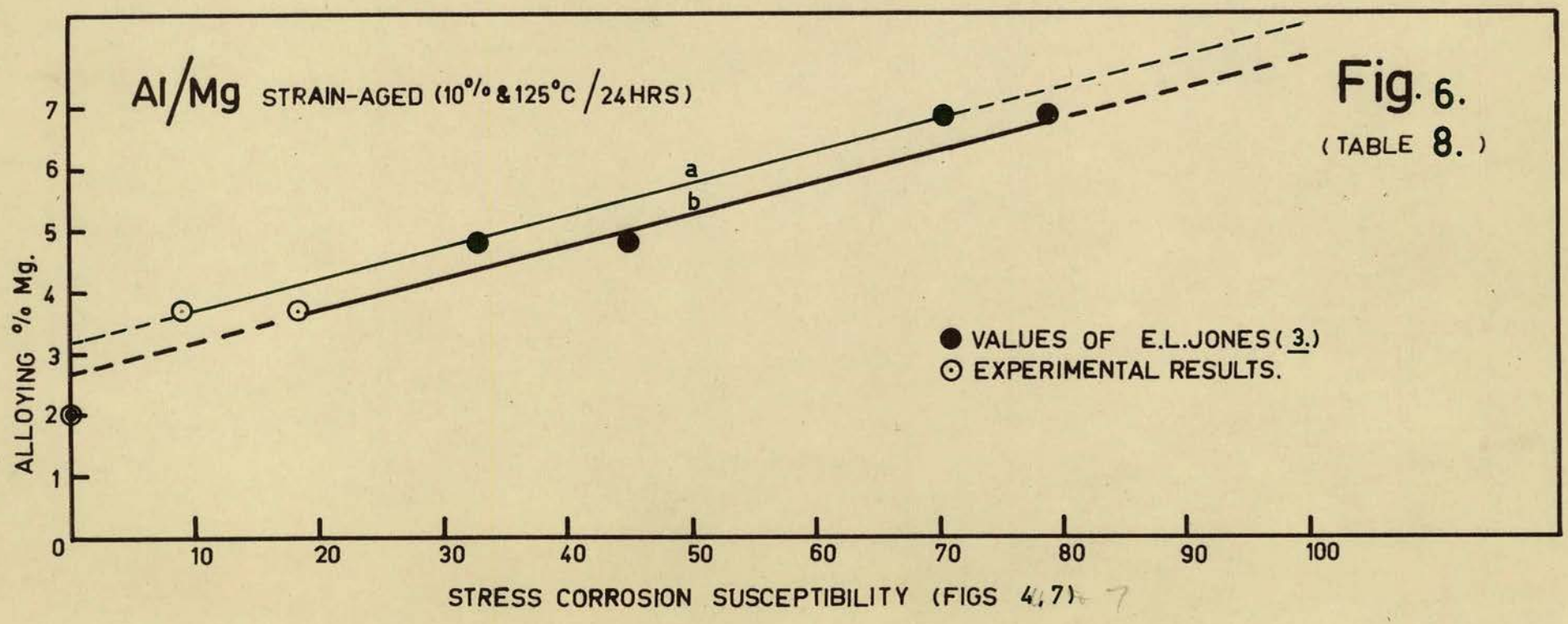


Fig. 6.

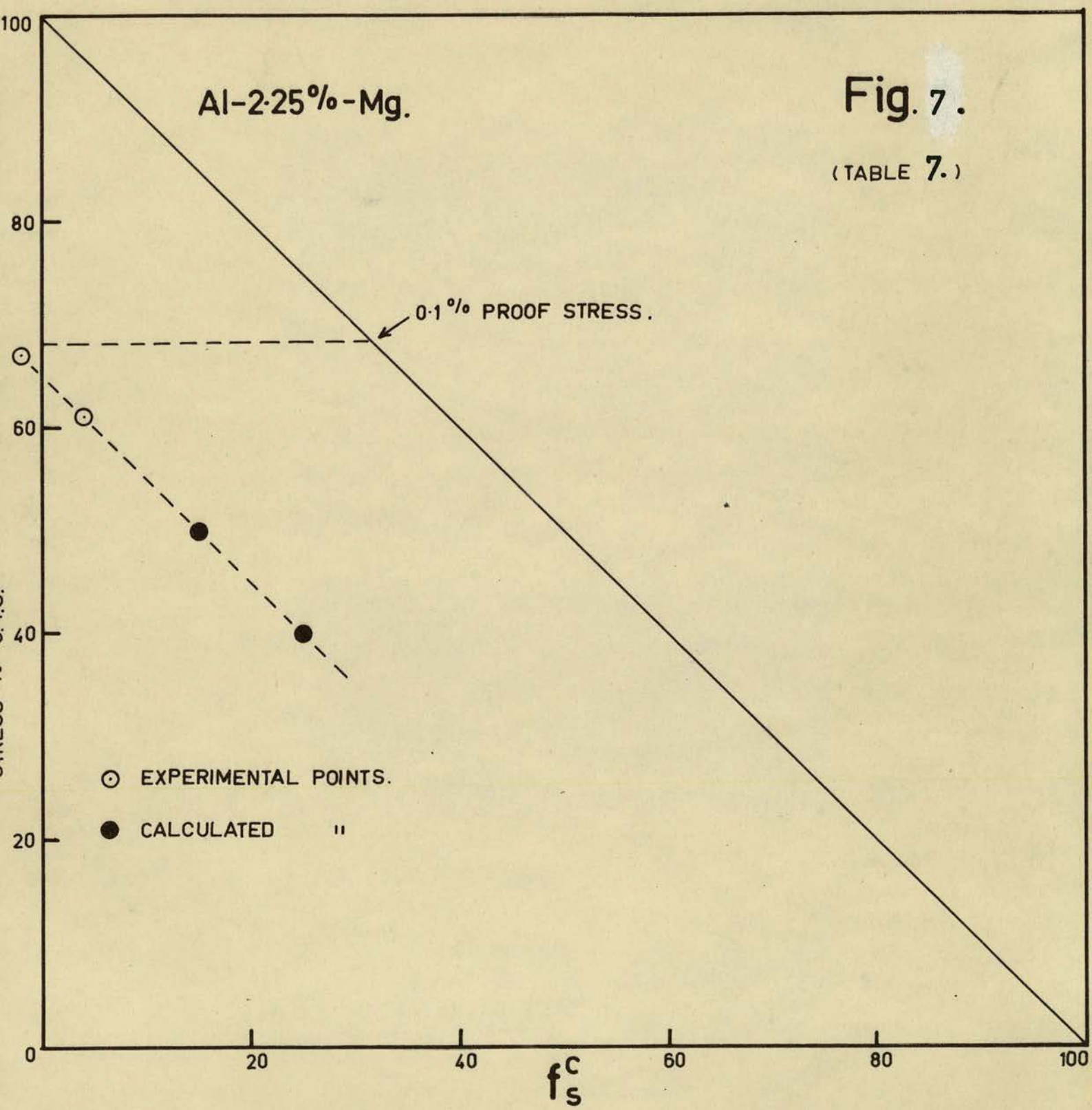
(TABLE 8.)

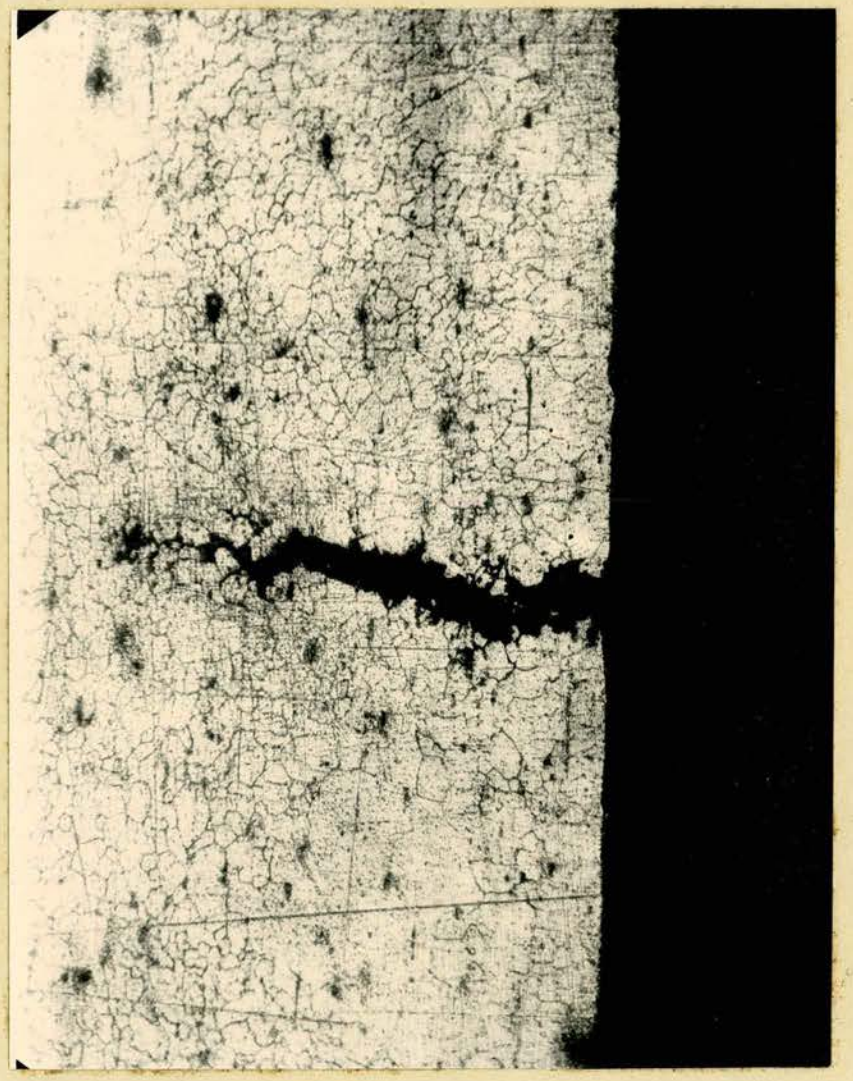
to the time axis. The spread of results is greater than that obtained with the 3½%-Mg alloy and corresponds with the lesser degree of visible signs of corrosion observed i.e. the later onset of tarnishing and the occurrence of shallower pits surmounted by a smaller amount of corrosion product.

When corroded under applied stresses of between 61% and 67% of the U.T.S. times to failure were greater than 260 hours and lay within the flat region of the unstressed curve. This being the case no more than 4 results were considered necessary since the derived value of S_u^c remained constant.

The value of S_u^c in the case of the 2¼%-Mg. alloy was constant at 35% for stresses up to 98.3% of the 0.1% proof stress and in consequence the plot of f_s^c vs. applied stress was linear intersecting the stress axis in the region of the proof stress. (Fig. 7, Table 7) It can be seen from Table 7 that the losses in % U.T.S. for both the stressed and unstressed conditions were similar and it was concluded that the stress-corrosion susceptibility of the 2¼%-Mg. alloy was nil.

The experimentally determined stress-corrosion susceptibilities of the 2¼%-Mg. and 3½%-Mg. alloys along with the values obtained by Jones (3) for the


Al-2·25%-Mg.
Fig. 7.
(TABLE 7.)
100
80
60
40
20
0
0·1 % PROOF STRESS.
EXPERIMENTAL POINTS.
CALCULATED "
20
40
60
80
100
f_s^c



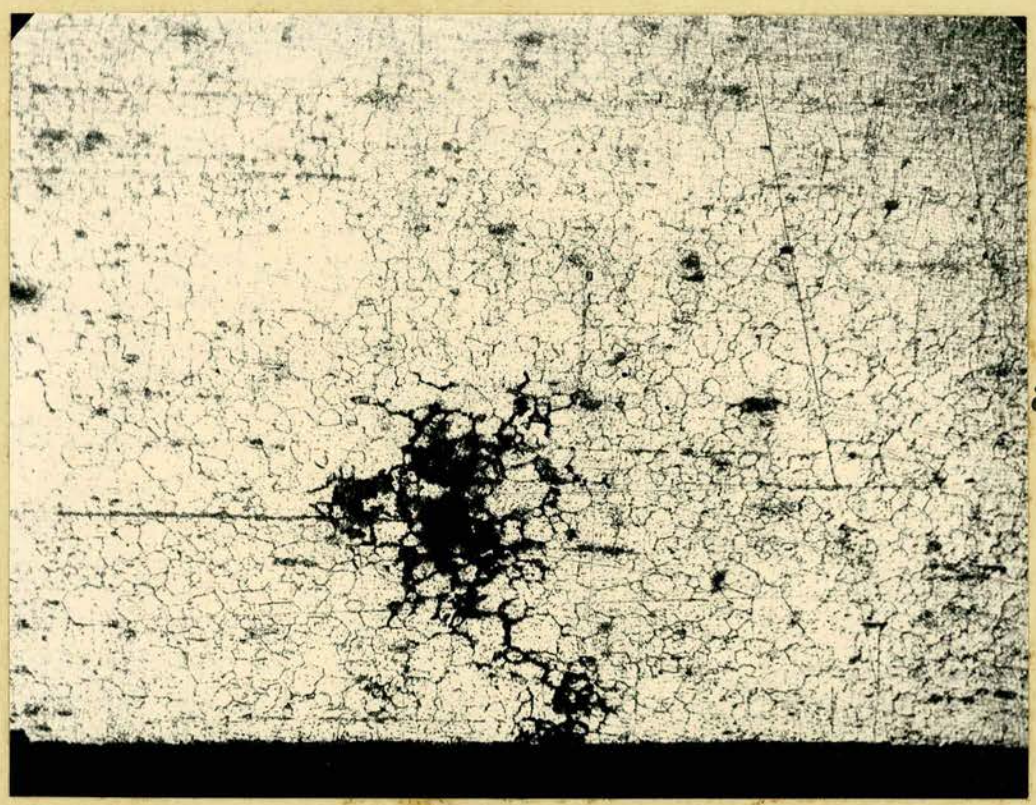
STRESS-CORROSION CRACK. X 175.
Al-3·5% Mg.

Fig. 8.

5%-Mg. and 7%-Mg. alloys were plotted against % magnesium content and a linear relationship was obtained. This is shown in Fig.6b and Table 8. The significance of the extrapolation of this curve is discussed later.

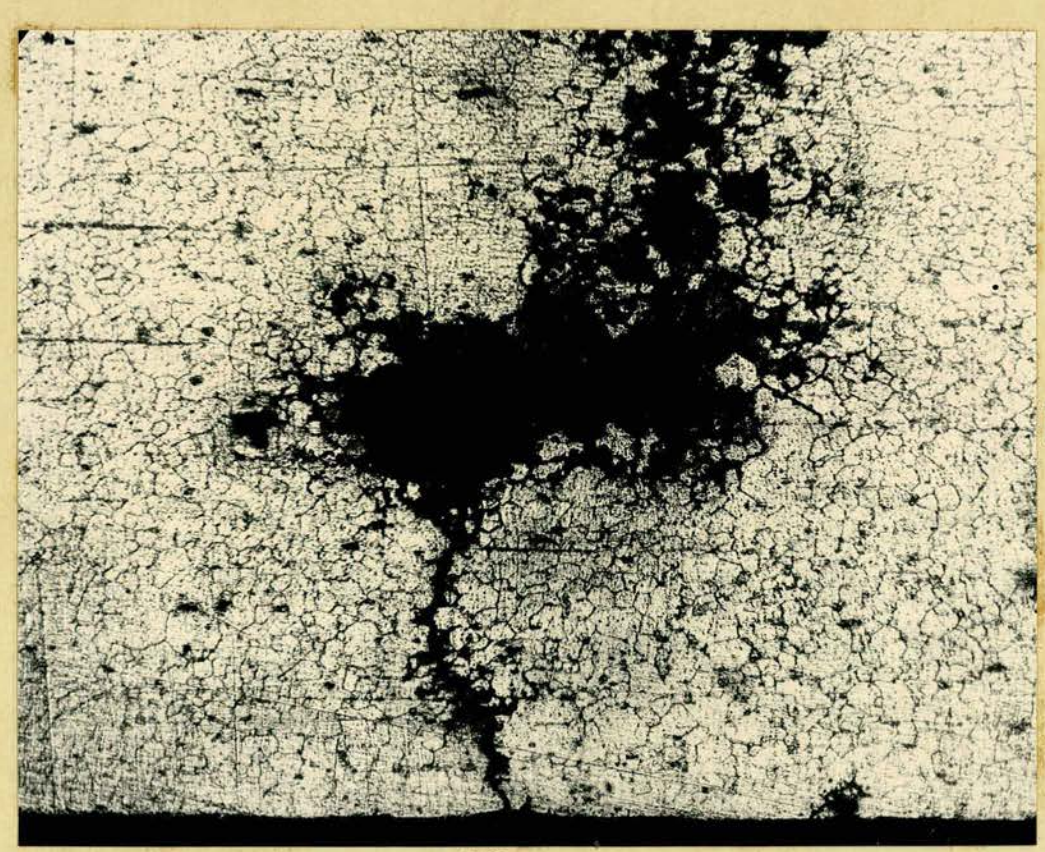
A typical intergranular crack in a stress-corroded specimen of Al-3½%Mg. which failed in 30 hours when corroded under an applied stress of 69.6% of the U.T.S. is shown in Fig. 8. The crack illustrates adequately the "yawning" phenomenon described by Edeleanu (4). No cracks were observed in any of the stress-corroded specimens of the 2¼%-Mg. alloy.

Figs. 9, 10 and 11 illustrate an unusual change of direction of intergranular attack which was observed in large numbers of specimens of Al-3½%-Mg. which had been corroded both in the stressed and unstressed conditions. The penetrative attack appeared to proceed radially for a short distance and then change to the axial and circumferential directions so that a macro-cross-section revealed a corroded annulus or part annulus immediately below the metal surface enclosing an unattacked core. A similar phenomenon has been described by Evans. (5).



a.

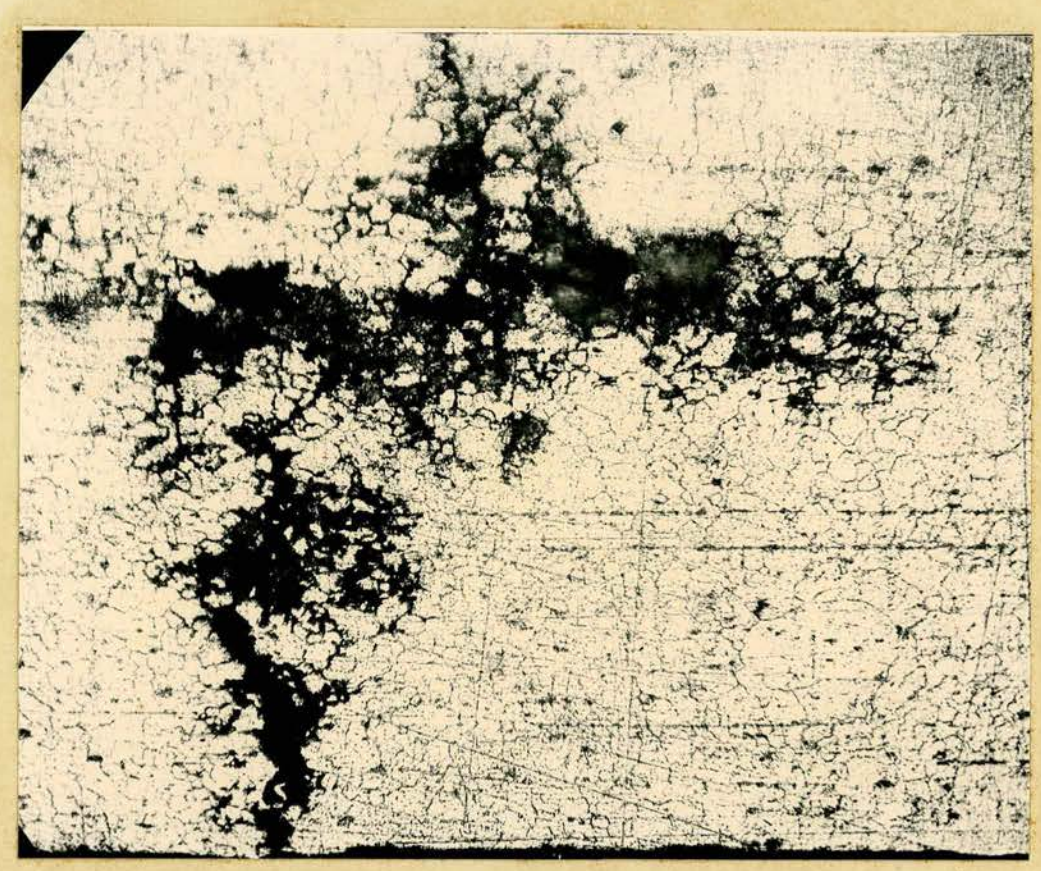
INTERGRANULAR CORROSION IN Al-3·5 %Mg. L.S. 16 S.W.G. WIRE.



b.

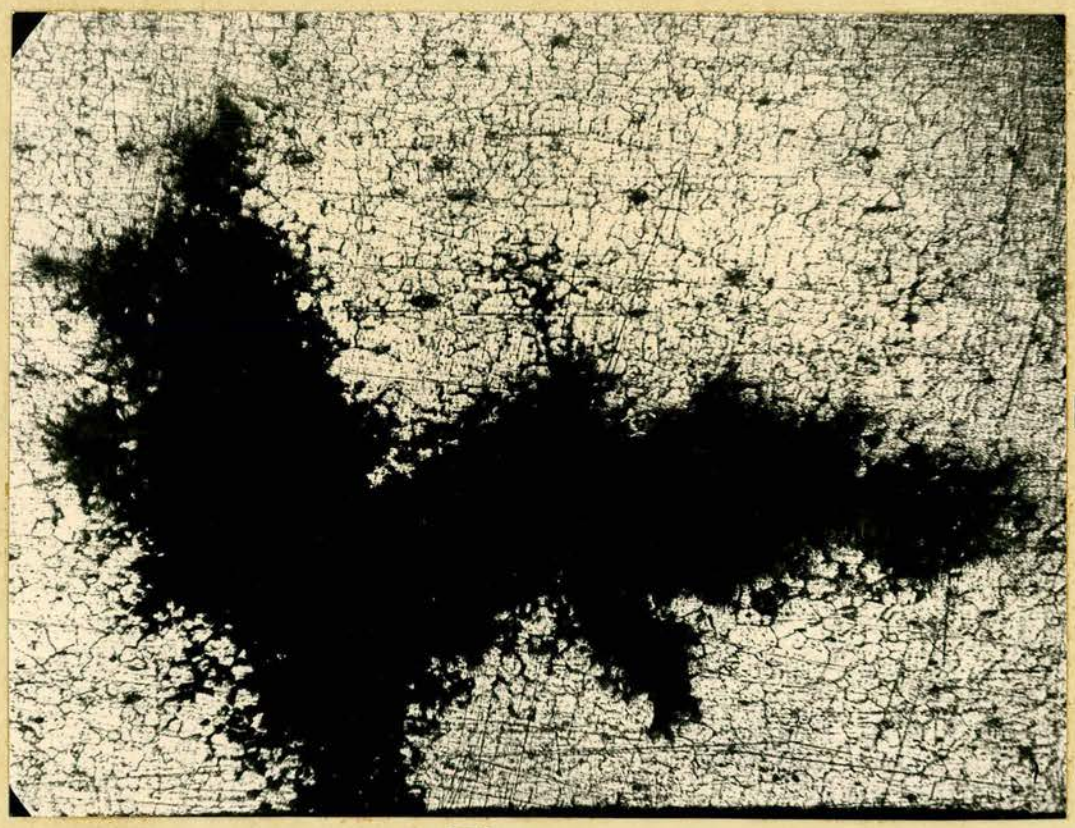
X 175.

Fig. 9.



a.

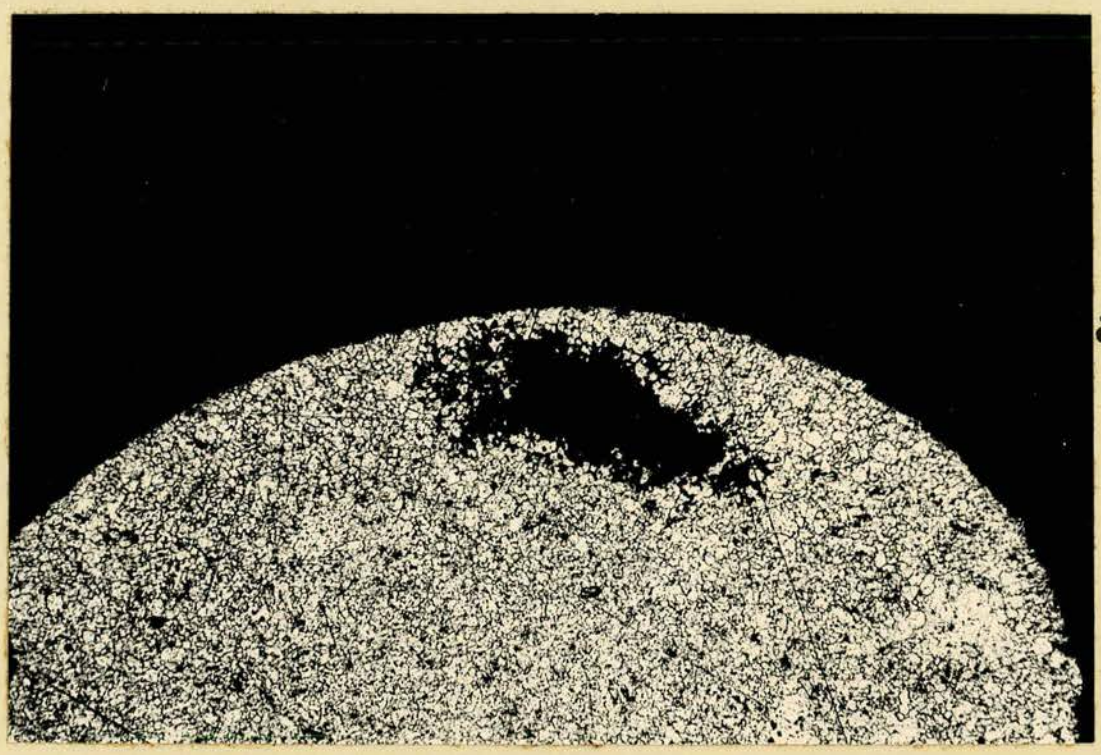
INTERGRANULAR CORROSION IN Al-3·5 %Mg. L.S.16 S.W.G. WIRE.



b.

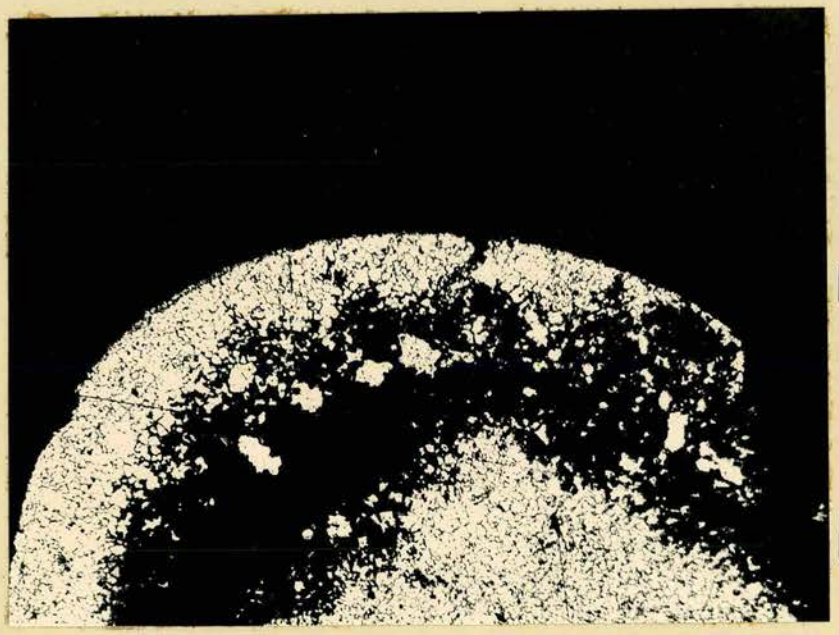
X 175.

Fig. 10.



a.

INTERGRANULAR CORROSION IN Al-3·5 % Mg. T.S. 16 S.W.G. WIRE.



b.

Fig. 11.

X 75.

DISCUSSION. Part I.

DISCUSSION. Part I. (See Experimental Part I.)

In accelerated stress-corrosion testing the quantitative aspect of the experimental results is largely governed by the nature and degree of the treatment which the "as received" specimens of commercial alloys undergo before they emerge as finished test-pieces. Reproducibility of results on the other hand depends on the close control of pretreatment which ideally should not vary in any respect from specimen to specimen. This is particularly true with respect to ageing which is a function of time and temperature and probably constitutes the most vital factor in the pretreatment of Al/Mg alloys inasmuch as it controls the degree and disposition of the precipitation of the β-phase, Al_3Mg_2. Precipitation at grain boundaries becomes more profuse and more continuous with increase in ageing time or ageing temperature. (92) The ageing time and temperature chosen in the experimental work described in this thesis were those used by Jones (2) in his work on the 5% and 7% Mg alloys and enabled comparison of the four alloys to be made on a common basis. The conditions were derived primarily, however, from

the work of Perryman and Hadden on Al-7%Mg which is reproduced in part in Fig. 46d. It can be seen that the ageing temperature of 125°C lies within the range of maximum stress-corrosion susceptibility.

Plastic deformation prior to ageing decreases the stress-corrosion life of Al/Mg alloys but the effect is much more marked for lower degress of overstrain as is shown by the curve of pre-overstrain vs. stress-corrosion life reproduced in Fig. 46f. For a given increment of overstrain the decrease in stress-corrosion life is greater for small overstrains than for large. The precipitation of Al_3Mg_2 takes place at more grain boundaries and is more continuous in the overstrained aged alloy than in the aged but not pre-overstrained material. The effect is not so marked at higher ageing temperatures. For example the stress-corrosion life of Al-7%Mg aged at 125°C for 24 hours has been reported to change from 113 days with 0% overstrain to 11 days with 2% pre-overstrain. The life of the same alloy aged at 200°C decreased from 2 days to 12 hours for 0% to 2% pre-overstrain. (94) i.e. a change from 10-1 to 4-1. The overall

reproducibility of experimental results obtained in the work described in this thesis was rather better than expected and it is believed that the care used in the preparation of the test-pieces and the close control of the corrosive environment were the main factors responsible.

The unstressed corrosion-time curve of the 3½%Mg alloy (Fig.3) is comparable to those obtained by Jones (2) and others (96) but shows a maximum of 48% loss of U.T.S. (at 280 hours) and thus falls between the curves of Al-5%Mg and Al-7%Mg reported by Jones, instead of below the 5% curve as might be expected. This displacement is discussed later. The stress vs. time-to-failure curve for this alloy is derived, as stated, from the means of larger than usual numbers of time-to-failure determinations and the spread of results and the high threshold stress suggest that with respect to stress-corrosion susceptibility the alloy is a border-line case. The curve is similar in form to those obtained by George and Chalmers (97) a typical example of which is reproduced in Fig. 46c. It can be seen that the curve becomes asymptotic to a sloping line which ultimately intersects the time axis. The sloping nature of the asymptote

has been remarked by Evans. (98).

The term threshold stress as used above has been defined as the lowest applied stress under which a susceptible alloy fails by stress-corrosion in a suitable corrosive environment. (2) It is felt that if the term "stress-corrosion cracking" were substituted for "stress-corrosion" the definition would give a more clear description of the stress vs. time-to-failure curve, since the apparent threshold stress of 52% U.T.S. suggests that no failures should be observed at lower applied stresses. Failures were in fact observed at stresses below 52% U.T.S. as shown in Table 4. These failures, although clearly due to pitting reduction of cross-section followed by necking and showing no evidence of cracking must nevertheless be classified as stress-corrosion failures since losses were incurred of 65% and 56% U.T.S. of which only 48% U.T.S. can be accounted for by unstressed corrosion. The following tentative explanation for these low stress failures is offered and is based on a possible acceleration of pitting corrosion caused by film failure at the bottom of pits. It is suggested that the film failure is caused by a series of

yields which take place during the stress-corrosion test due to reduction of cross-section by pitting corrosion.

Let the U.T.S. of the test specimen = $U.T.S._1$

Then the initial 0.1% proof stress = 74% $U.T.S._1$

Unstressed corrosion-time curve

max. (280 hrs.) = 48% loss $U.T.S._1$

∴ Residual U.T.S. at 280 hrs. = 52% $U.T.S._1$ = $U.T.S._2$

If the relationship 0.1% proof stress = 74% U.T.S. holds throughout the length of the unstressed curve:-

Then 0.1% P.S. at 280 hrs. = 74% $U.T.S._2$ = 38.5% $U.T.S._1$

= $P.S._2$

∴ the applied stress of 43.5% U.T.S. = 113% $P.S._2$

and 38.4% " = 90.3% "

With regard to duralumin Champion (99) has shown that proof stress is unaffected by corrosion until the residual U.T.S. approaches the initial proof stress. At this point loss of proof stress begins and accelerates rapidly until the residual U.T.S. reaches the value of the initial

proof stress. From here onwards the ratio of the residual proof stress to residual U.T.S. remains at 0.9 as corrosion proceeds. For Al-7%Mg he showed that when the loss of U.T.S. reached 57% the loss of proof stress was 45%. It is a reasonable assumption that Al-3½%Mg behaves in a similar fashion and hence the value of $P.S._2$ shown above will be reduced to ca. 60% of 38.5% or 23% $U.T.S._1$. If this is true then yielding must have taken place at both the applied stresses of 43.5% and 34.8% U.T.S. and at some time earlier than 280 hours. From the unstressed curve it can be seen that the residual U.T.S. reaches the initial proof stress at ca. 100 hours and it is suggested that a series of yields began at or about this time accompanied by (a) film failure with acceleration of normal corrosion at the bottom of the pit which caused the final critical reduction in cross-section and/or (b) changes in the corrosion characteristics of the alloy at the point of yielding so that greater losses than are shown by the asymptote of the unstressed curve were incurred.

When this argument is used for applied stresses at and above the threshold stress (52% U.T.S.) it can be seen from Table 4 that the average

time-to-failure at the threshold stress was 116 hours and that if one abnormally high value of 232 hours be excluded from the average this would then fall within the time (100 hours) required for the residual U.T.S. to reach the initial proof stress, i.e. failure by cracking took place before yielding due to reduction of cross-section by pitting occurred. Furthermore if applied stress below the threshold stress has little effect on the initial stage of corrosion, then the time for the residual U.T.S. to reach the initial proof stress is independent of load. From this point according to Champion the loss of proof stress accelerates and if the rate is high the yields due to the applied stresses of 43.5% and 34.8% U.T.S. may take place within a short time of one another. Again if the nature of further corrosion is still the normal pitting type, failure-times for the two loads should be somewhat similar. The failure times were in fact 376 and 399 hours respectively.

Applying the same argument to the 2½%Mg alloy it can be seen that:-

Initial 0.1% proof stress = 68.3% U.T.S.$_1$

Unstressed corrosion-time curve max. (260 hrs) = 35% loss U.T.S.$_1$

$\therefore$ Residual U.T.S. at 260 hrs. = 65% $U.T.S._1$

= $U.T.S._2$

If the relationship 0.1% proof stress holds throughout the length of the unstressed curve:-

then the 0.1% P.S. at 260 hours = 68.3% $U.T.S._2$

= 44.4% $U.T.S._1$

= $P.S._2$

$\therefore$ the applied stresses of 67.1% U.T.S. = 151% $P.S._2$

61.0% " = 137% "

From the unstressed curve it can be seen that the residual U.T.S. = initial 0.1% proof stress at 240 hours, at which time according to Champion rapid loss of proof stress occurs. A series of yields probably began at or about this time. Once again for reasons given in the case of the 3½%Mg alloy failure for both applied stresses took place at approximately the same time, i.e. 360 and 390 hours respectively.

The U.T.S. and 0.1% proof stress of both alloys were determined by the constant load method and during testing large yields were observed in both materials particularly just after the 0.1% P.S. had been reached. McReynolds (100) has shown that

in alloys of aluminium with copper or magnesium, plastic deformation proceeds in step fashion rather than at a constant strain rate and found that the effect depended on the presence of the Cu. or Mg, and was absent in aluminium of 99.99% purity. Lubahn (101) states that if a metal is ageing while being plastically deformed it may exhibit such unusual deformation characteristics as (a) discontinuous yielding in tensile tests, (b) periodic sudden extensions in a constant load creep test and (c) failure ever to undergo gradual extension at constant load. Phillips, Swain and Eborall (102) have in fact shown that the stress-strain curve of Al-3½%Mg proceeds in steps after about 0.75% extension which is only a very small fraction in terms of stress from the 0.1% proof stress in Al/Mg alloys. These reports lend some support to the suggested mechanism of sudden yielding during prolonged exposure to corrosion at stresses below the threshold stress.

The unstressed corrosion-time curve of the 2½%Mg alloy shows a much longer induction period than those of the higher magnesium content alloys. Like the curve of the 3½% and 5% materials it becomes asymptotic to the time axis but at a lower

%loss of U.T.S. (Fig.5). It is perhaps significant that the unstressed corrosion-time curves of both Al-2¼%Mg and Al-3½%Mg flatten out after approximately the same period of exposure to corrosive conditions as do those of the 5%Mg and 7%Mg reported by Jones. (2) All four alloys were manufactured at the same time and under identical conditions. The respective curves flatten out after 260, 280, 300 and 280 hours. It is suggested that the form of these curves is governed by two major factors:-

(1) The value of the maximum is a function of the composition which determines the rate at which the alloy reacts with the corrosive solution. The rate (for constant wire diameter) is indicated by the slope of the curve between the end of the induction period if any and the asymptote. The above presupposes identical pretreatment of the alloys from the moment of manufacture, i.e. commercial annealing, overstraining and ageing, etc.

(2) The cessation of further corrosion at the asymptote is caused by the build up of film whose quality and thickness increases with time at a rate which appears to be independent of the alloy composition, i.e. with respect to Mg content. The

% loss of U.T.S. which takes place during the time required for the build up of the film will depend also on the specimen thickness.

Unstressed specimens removed from the corrosive solution after exposures of greater than 100 hours were observed to be coated with a gelatinous external film whose bulk was greatest in the region of pits. This film was easily removed by mechanical washing and revealed a second compact and hard film which could not be removed in this way. If the specimens were dried and then bent the hard film flaked off. The experiment described in Experimental Part I, in which the unstressed corrosion-time curve of the 3½%Mg alloy was reconstructed while removing the film every 24 hours, showed that this film did not appear to influence the final form of the curve. (Fig. 20) It is suggested that, while removal of external film was carried out, the film at the base of pits was probably left untouched by the technique of removal. It is probably the building up of this film at the bottom of pits (which are the points of active attack) which determines the time at which the curve becomes asymptotic to the time axis.

The change of direction of intergranular attack in Al-3½%Mg, illustrated by Figs. 9, 10 and 11,

is of interest in this connection because it results in comparatively large pockets of active corrosion which are isolated from the outside surface of the specimen. It is clear from the sections shown that the removal of corrosion films formed within these cavities would not be possible by the removal technique used; and these films are the most important as far as the stifling of corrosion is concerned since they are present at the points of active attack of the alloy. Evans has associated the abnormally long life (i.e. abnormal compared with the average life) of certain specimens, presumably rolled plate, with this phenomenon of change of direction of attack (98) and two results shown in Table 4 of this thesis of 93.5 hours (exclusive average = 28.5) and 321 hours (exclusive average = 34.7) lend support to this theory.

The stress-corrosion susceptibilities of the 2¼%Mg and the 3½%Mg alloys as estimated by the method of Jones (3)(and shown in Figs. 7 and 4 and Tables 7 and 5) were 0 and 18.4 respectively. The susceptibilities of the 5% and 7% Mg alloys obtained by Jones were 45 and 79 respectively. Stress-corrosion susceptibilities were plotted

against alloying % of magnesium for the four alloys as shown in Fig. 6, Table 8 and a linear relationship was obtained. The extrapolation of the curve to 100% susceptibility indicated an alloying % of magnesium of 8 corresponding to this value. The marked decrease in the solubility of magnesium in aluminium at lower temperatures (Fig. 47 and (32, 86, 87.) indicates that alloys containing more than 1.9% Mg should show a progressive response to age-hardening by virtue of the precipitation of the β-phase, Al_3Mg_2, on reheating the homogenised alloys at lower temperatures. Vachet (88) states however that he found difficulty in precipitating β-phase from solid solutions containing less than 8% Mg. Thus equilibrium (i.e Mg% = 3.6-4.0 at 200°C) was reached in two days with a 12% Mg alloy whereas 8 days were required to reach the same equilibrium with the 8% alloy. In view of this evidence it is suggested that within the strict limits of the experimental conditions described herein the value of 100% stress-corrosion susceptibility for comparable alloys of 8% Mg is not unreasonable. Further evidence in favour of this conclusion is available as follows:-

(1) During the ageing of Al-7%Mg precipitation takes place first at grain boundaries (89) and metallographic examination indicates that this holds for similar alloys of different magnesium content. (85)

(2) Cold work before ageing causes precipitation to take place at more grain boundaries than would occur if the alloy were not preoverstrained. (90)

(3) If the ageing temperature of overstrained Al-7%Mg is raised from 125°C to 212°C for the same ageing time, grain boundary precipitation is fragmentary and dense precipitation occurs within the grain bodies. At the same time stress-corrosion life increases by a factor of over 100. (91)

(4) It has been shown that when β-phase precipitation takes place selectively at grain boundaries there exists a difference in potential between the boundaries and the grain bodies, the β-precipitate being anodic. (85).

A progressive degree of β-phase precipitation can be visualised in which the amount of β-precipitate formed by strain-ageing is controlled by the degree of saturation of the solid solution. This is

measured by the solubility of magnesium in aluminium at normal temperature (1.9%, Fig. 47.) and the alloying % of magnesium in the alloy. This means that for similar alloys of different Mg content the amount of β-phase precipitation is proportional to the alloying % Mg for the same strain-ageing treatment. Since precipitation takes place first at grain boundaries one can imagine a progressive increase in the density of β-precipitate at grain boundaries in a range of similar alloys of increasing Mg content from 2-8% until the boundary zone becomes "saturated". With alloys of higher Mg content the boundary zone becomes rapidly "saturated" but there is an overflow of β-precipitate which now takes place in the grain body. The ultimate stage is achieved when the Mg content of the alloy is such that β-precipitation takes place to the same extent throughout the entire alloy. (74, Plate X.) In this condition there is no longer any anodic path along the grain boundaries since the potential difference between the previously anodic boundary precipitate and the cathodic grain body has been destroyed by the removal of anodic material into the cathodic region, i.e. the grain body. In this condition the alloy would be theoretically

non-susceptible to stress-corrosion. Intermediate stages can be postulated in which the anodic character of the grain boundary is partially balanced by β-precipitate present in the grain body. In these cases a lesser degree of selective anodic attack than the maximum possible will probably take place and the stress-corrosion susceptibility will be somewhat less than 100%. The maximum condition of stress-corrosion attack should be observed when the grain boundary zone is "saturated" with β-phase precipitate and the grain body remains precipitate free. In this case the maximum potential difference will exist between the grain body and the boundary zone. It is suggested that the latter conditions probably exist at an alloying Mg% of 8.

The mechanism as described may not be so sharply defined but there appear to be reasonable grounds to suppose that in Al/Mg alloys susceptibility to stress-corrosion increases with magnesium content upwards of 2% and reaches a maximum at 8% Mg. For higher Mg contents the probability exists that the susceptibility will tend to decrease. At the other extreme, since the solubility of magnesium in aluminium is 1.9% at normal temperature, the suggested zero susceptibility of the 2¼%Mg alloy

(actually 2.01%Mg, Table 1.) is feasible on the grounds that a high enough degree of β-precipitation at grain boundaries is not likely at such a low state of supersaturation.

Data reported by Dix (66) and reproduced in Fig. 48 are of considerable interest in connection with the above argument. The work was carried out on Al/Mg sheet, cold rolled 50% and aged at 100°C for four hours. Uniformly stressed cantilever specimens were loaded by dead weight to ¾ of the yield strength and totally immersed in NaCl-H_2O_2 solution. An anodic potential of 0.9 volts was applied to each specimen and those which failed under these conditions were considered susceptible to stress-corrosion. It is not easy to compare the stringency of the conditionsof Dix with those described in Experimental Part I but it is generally agreed that intermittent immersion is more severe than total immersion. The results reported herein on Al-3½%Mg also suggest that the overall severity of the author's conditions was greater than that of the conditions used by Dix. It is felt that if the work of Dix were repeated using the method of intermittent immersion and alloy specimens aged at 125°C for 24 hours the final curve would be displaced

to the left, to include within the probability of stress-corrosion, alloys containing ca. 3% Mg with a corresponding increase in probability for higher Mg % alloys. Comparison is made more difficult because of the need to interpret the curve in terms of the ratio of failures to nonfailures in groups of specimens. The derivation of stress-corrosion susceptibilities from the plot of f_s^c vs. applied stress can be criticised on the grounds that the area enclosed by a line drawn horizontal to the f_s^c axis at the value of the proof stress expressed as %U.T.S. is included in the value of the susceptibility. This gives rise to the unsatisfactory situation that when the f_s^c vs. applied stress curve intercepts the stress axis at a value which is slightly less than the proof stress in terms of %U.T.S. then the whole area enclosed by the curve is taken as an estimate of the susceptibility. If however an alloy is found to be non-susceptible to stress-corrosion when stressed to 100% of the proof stress then the estimated susceptibility is zero and the area above the proof stress is ignored. An example of this is shown in Fig. 7. It is felt that a more valid comparison is obtained if the area above the proof stress is

not included in the value of the susceptibility. This has been done for the susceptibilities obtained by Jones (3) for Al-5%Mg and Al-7%Mg and for the susceptibility of Al-3½%Mg shown in Fig. 4. The value for Al-2¼%Mg remains unaffected. The corrected susceptibilities were plotted against alloying Mg % as shown in Fig. 6a. Extrapolation of the curve indicates limiting magnesium contents of 3.2% and 8.3% for zero and 100% susceptibility respectively. These values are probably more reliable than those shown by curve (b), Fig. 6, but the difference does not affect the argument based on the latter values.

EXPERIMENTAL Part II.

EXPERIMENTAL Part II.

COMPARISON OF THE METHODS OF INTERMITTENT IMMERSION AND SPRAYING.

Materials and preparation of test-pieces.

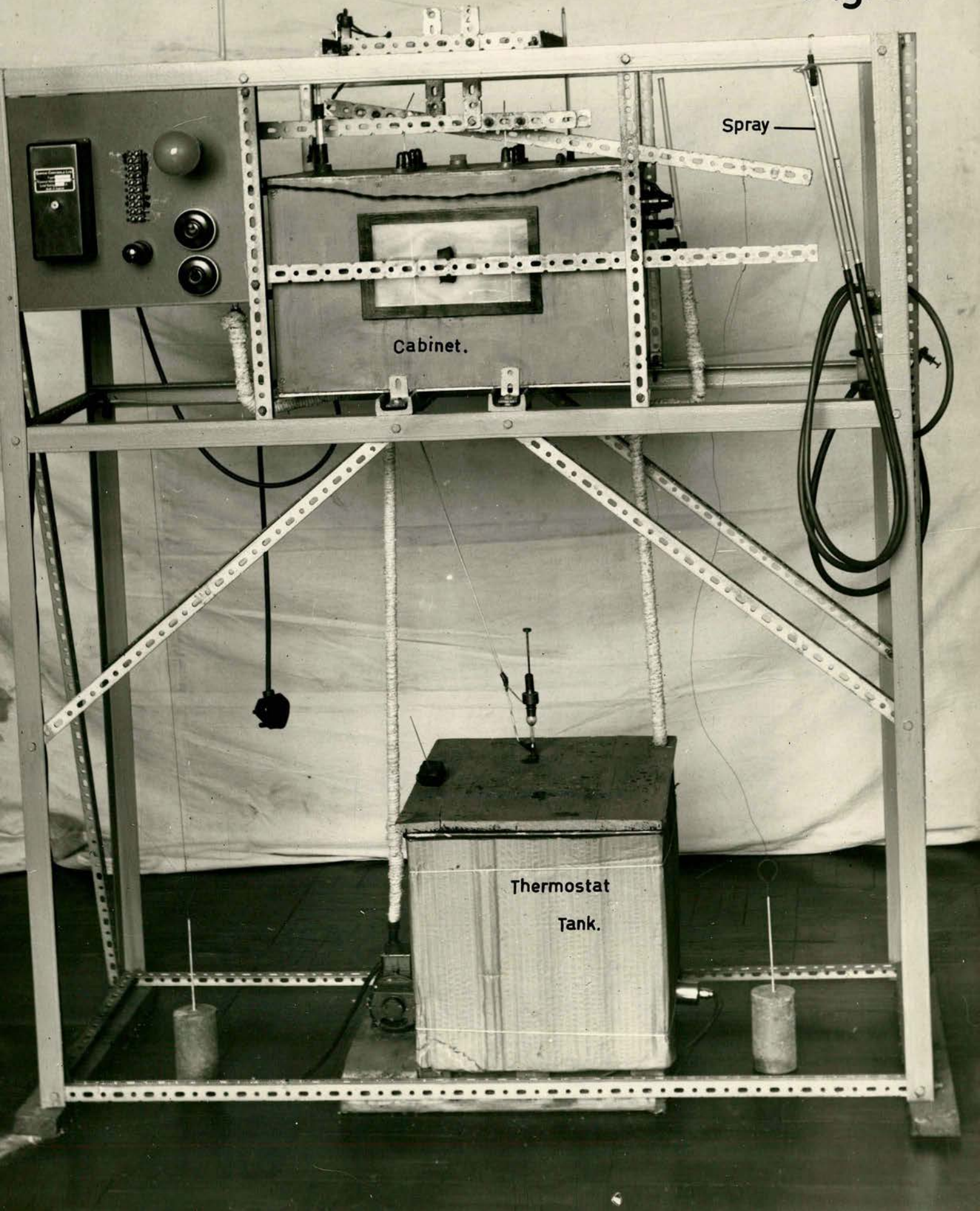
In order to compare the methods of intermittent immersion and spraying, Al-3½%Mg and Al-7%Mg alloys were selected since it was considered that their behaviour under the experimental conditions would be representative of the four commercial alloys available in this country. Test-pieces 19 inches long were cut from coils of 16 S.W.G. commercially annealed alloy wire, linearly overstrained 10% and aged at 125°C for 24 hours. (1,2.) Fig. 46f. The wires were cleaned, degreased and resin coated as before so as to provide 7 inch lengths for exposure to the corrosive environment.

Apparatus and Method of Testing.

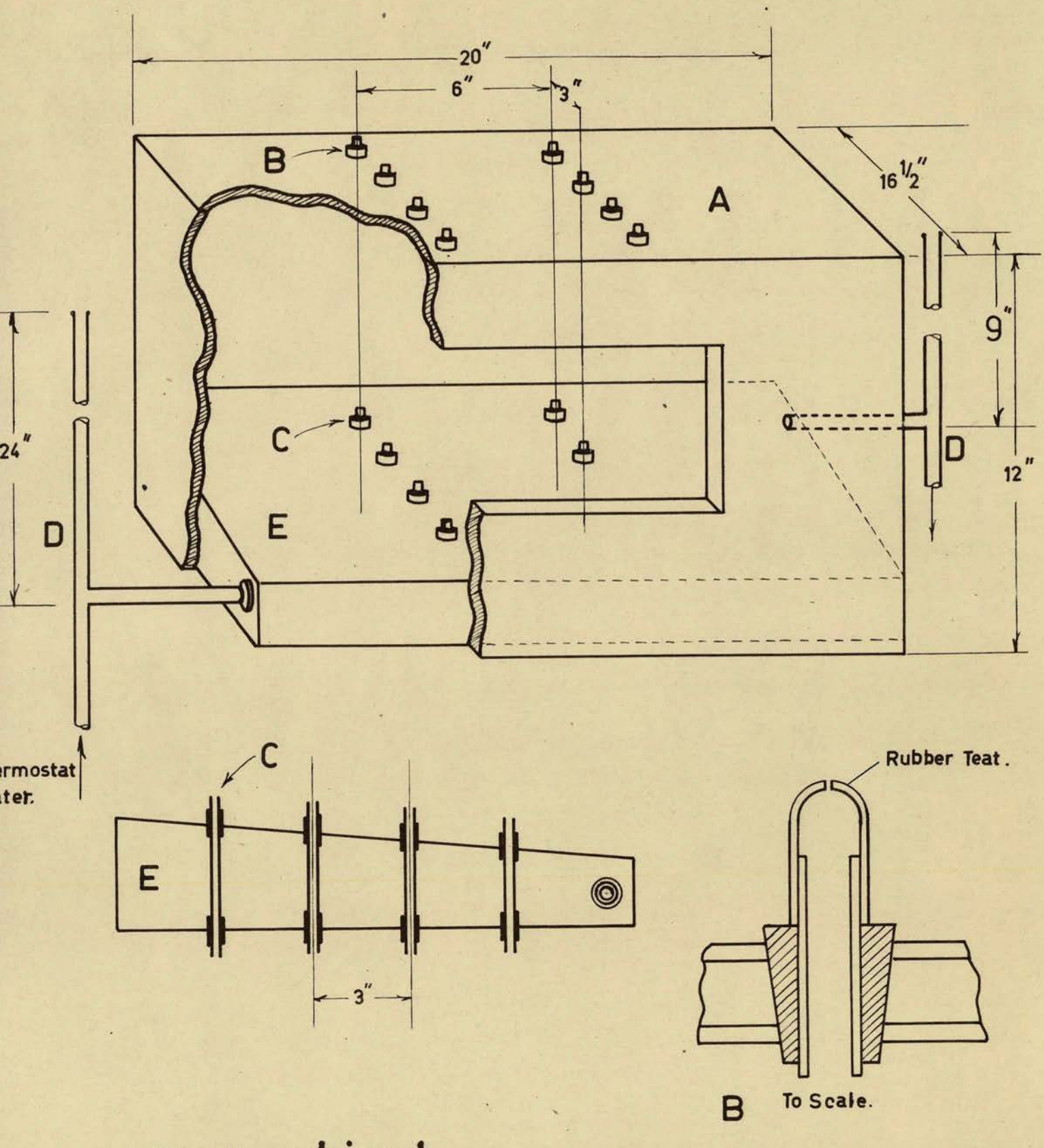
The apparatus consisted mainly of a thermostated air-tight cabinet in which test wires were sprayed with corrosive solution while in the stressed and unstressed conditions. The cabinet was constructed of double walls of ⅛ inch hardboard

SPRAY APPARATUS.

Fig. 12.



containing sheets of ½ inch felt. The inside floor which sloped down to the front to facilitate drainage was formed by the top of a perspex water-box. Within the box water at 25°C from a thermostated tank was constantly circulated by means of a pump so that the entire bottom of the cabinet functioned as a heating element. In this way convection currents from localised overheating were avoided. The perspex box was sealed into the bottom of the cabinet with plastic wood and the walls and cement were painted over with five coats of black cellulose paint. Within the cabinet no metal other than the test-wires was exposed in order that there should be no contamination of the corrosive solution films by foreign metal ions. The cabinet rested on channel irons which formed the anchor for the lower ends of the test-wires. The latter were passed through the cabinet through eight pairs of ¼ inch I.D. glass tubes, eight tubes passing vertically through the floor-box and the other eight through the roof of the cabinet. The tubes were sealed by means of feeding bottle teats, the top tubes on the outside and the lower tubes on the inside at the cabinet floor level. Test-wires were clamped in steel block vises, passed through



spray cabinet.

Scale 1/4.

Fig. 13.

the channel iron, through the lower teat seals and, after passing through the upper seals were clamped to the steel-yards. The cabinet was fitted with a heat insulated inspection light, an air thermometer and a double perspex door. Humidity was controlled as far as possible by the exposure of a large shallow dish of corrosive solution within the cabinet. Fig. 12 is a photograph of the apparatus as used. For details of construction see Fig. 13. The intention of the design and construction was to supply an environment in which the composition of spray droplets adhering to test-wires should remain unchanged from the time of deposition until the end of a test which was either the failure of a stressed wire or in the case of unstressed specimens the ending of a predetermined period of exposure. The spray nozzle was constructed of glass and was of the positive pressure atomising type. The pressure was supplied by the laboratory air main and the lengths of both the air and solution tubes was such that the spray unit was mobile and easily manipulated by hand. For details see Fig. 12.

Wires were passed through the cabinet with and without the application of stress and were sprayed twice daily for approximately ten seconds. The

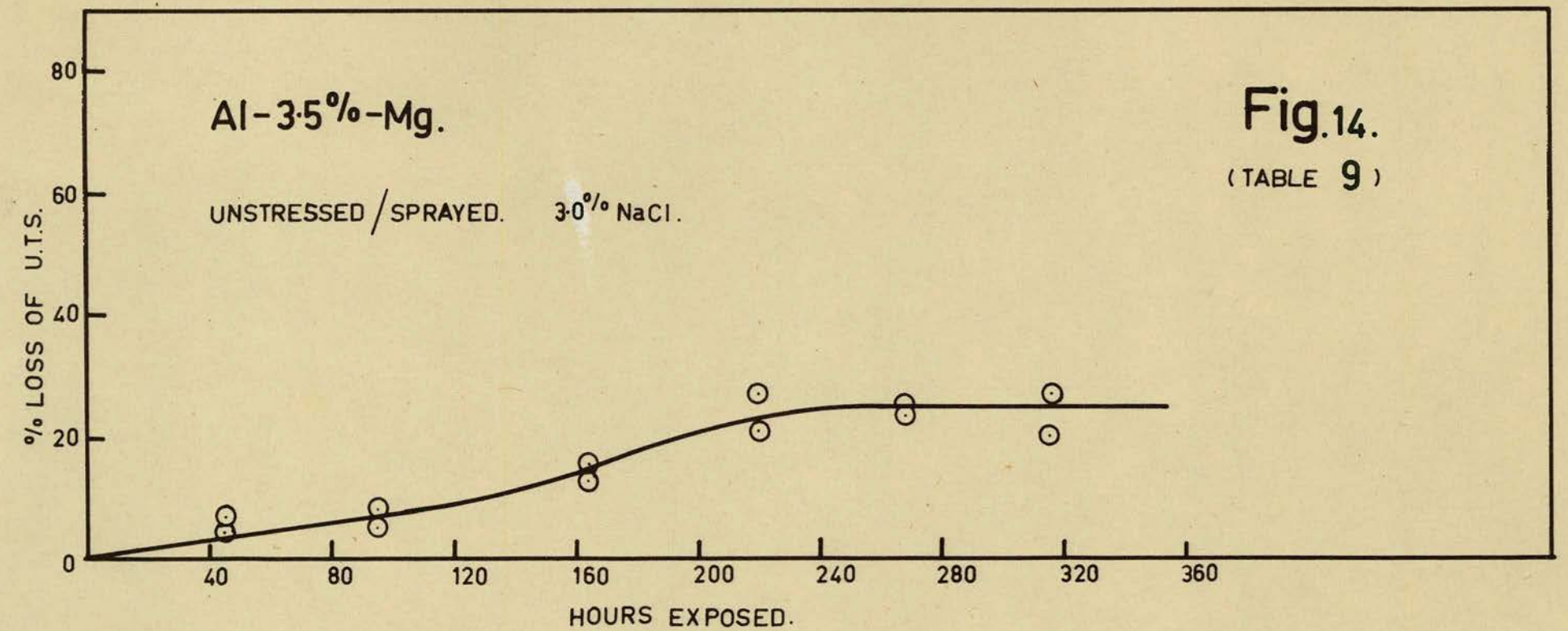


Fig.14.
(TABLE 9)

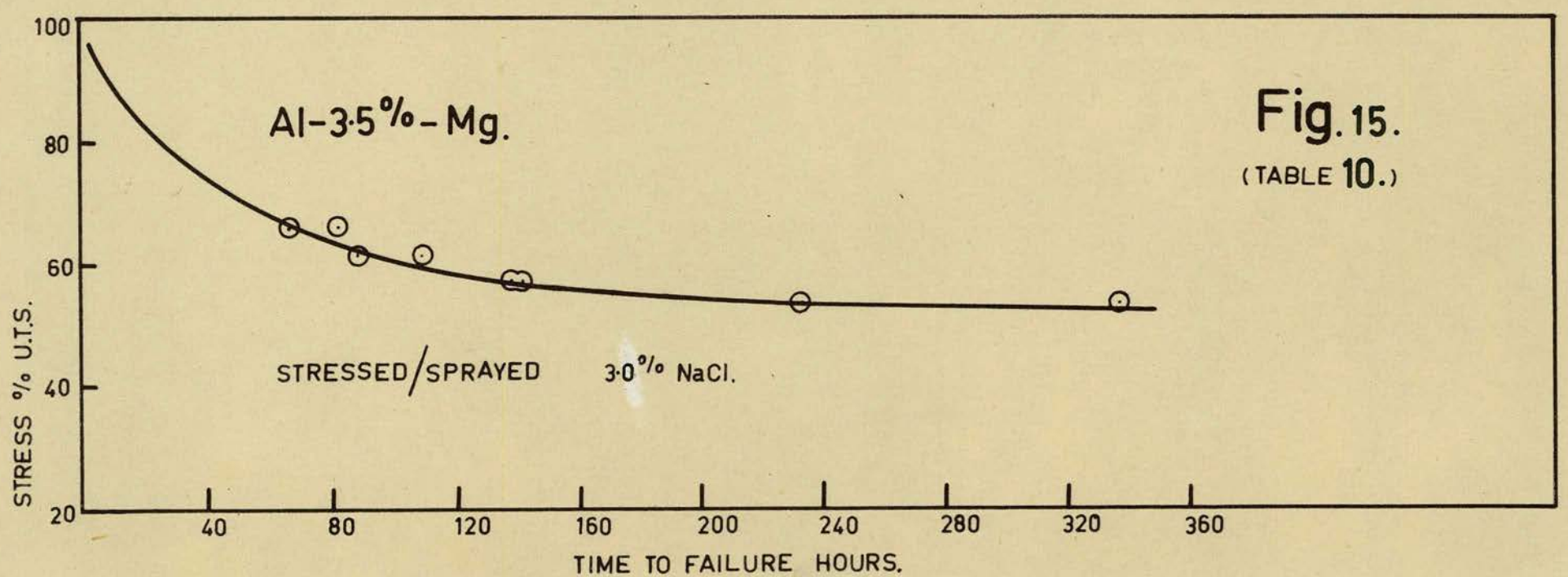


Fig.15.
(TABLE 10.)

nozzle was passed on either side of the rows of wires during spraying and, while being withdrawn, was directed into the centre of the cabinet as the door was closed. As far as possible the same technique was used each time the spray was applied. Stress was applied by means of weighted steel-yards erected over the cabinet and times-to-failure were recorded on electric stop-clocks operated by time-switches. In the case of the 3½%Mg alloy results of tests by the method of intermittent immersion described in Experimental Part I were used for comparison of the methods whereas intermittent immersion tests on the 7%Mg alloy were carried out simultaneously with the spray tests.

In order to examine the apparently anomolous relative position in the series of the intermittent immersion unstressed corrosion-time curve of the 5%Mg alloy reported by Jones (2) spray tests were later carried out on this alloy.

Experimental Results.

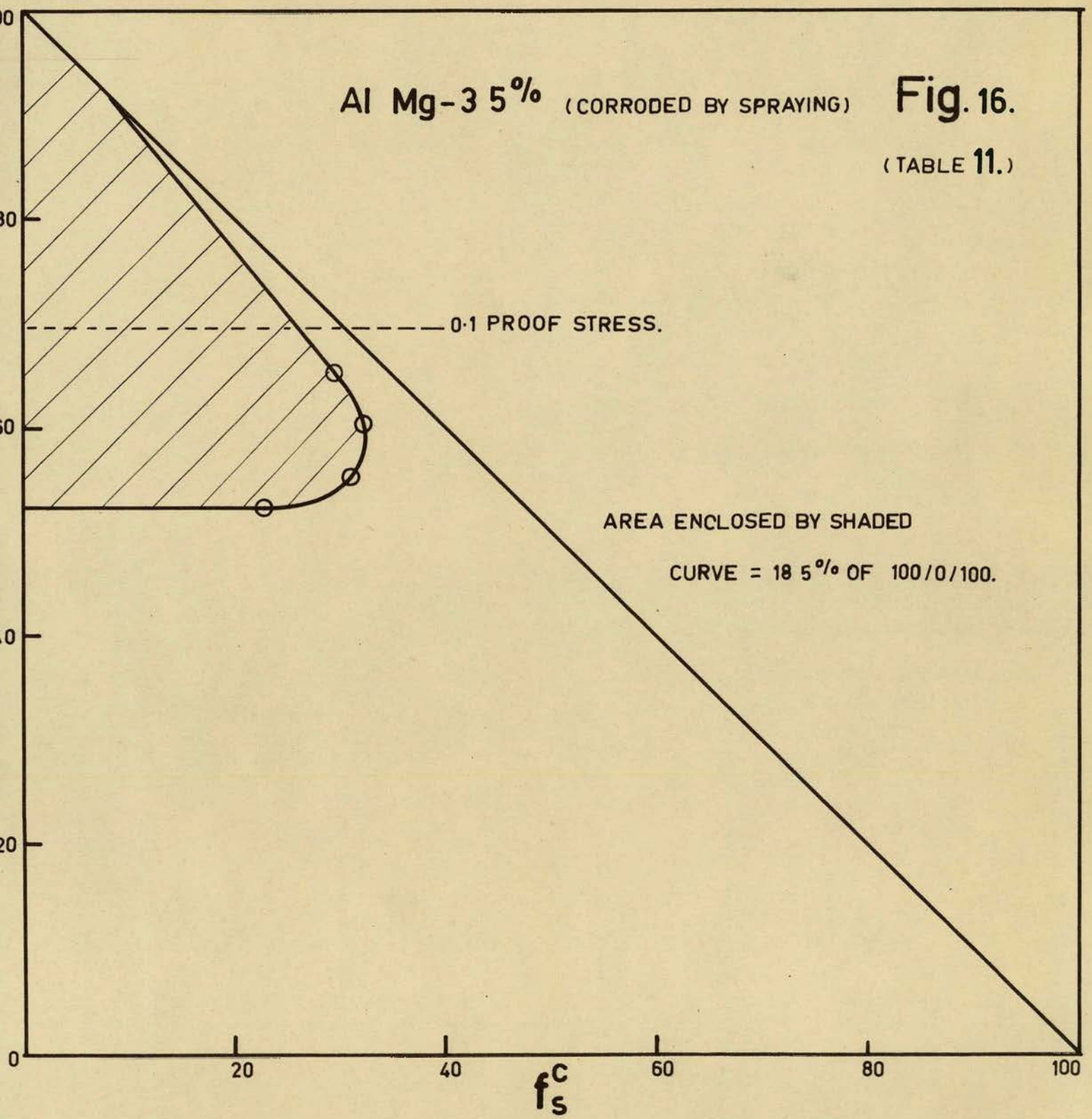
(a) Aluminium-3½%-Magnesium.

The unstressed sprayed corrosion-time curve is shown in Fig. 14 (Table 9). The curve shows an induction period of about 120 hours and then becomes

asymptotic to the time axis at 220 hours at a maximum loss of U.T.S. of 25%. There is a marked similarity to the unstressed corrosion-time curve of the 2¼%Mg alloy derived from intermittent immersion tests.

The applied stress vs. time-to-failure curve is shown in Fig.15 (Table 10) and can be seen to be considerably shallower than the intermittent immersion curve for the same alloy. The curve of applied stress vs. f_s^c is shown in Fig. 16 (Table 11). The stress-corrosion susceptibility determined by the method of spraying was 18.5%. (cf. intermittent immersion 18.4%).

The spray determined unstressed corrosion-time curves for 3½%Mg and 5%Mg alloys are shown in Fig. 23 (Table 18) and for the purpose of comparison the curve of Fig. 3 and the intermittent immersion unstressed corrosion-time curve for Al-5%-Mg obtained by Jones (2) is included. It can be seen that the differences between the maxima obtained by the two methods are similar in spite of the fact that the 5%Mg curve appears to be displaced below that of the 3½%Mg alloy. The displacement is thought to be due to a difference in the cooling gradients during the respective commercial solution treatments.


Al Mg-3 5% (CORRODED BY SPRAYING)
Fig. 16.
(TABLE 11.)
0·1 PROOF STRESS.
AREA ENCLOSED BY SHADED
CURVE = 18 5% OF 100/0/100.
0
20
40
60
80
100
f_s^c

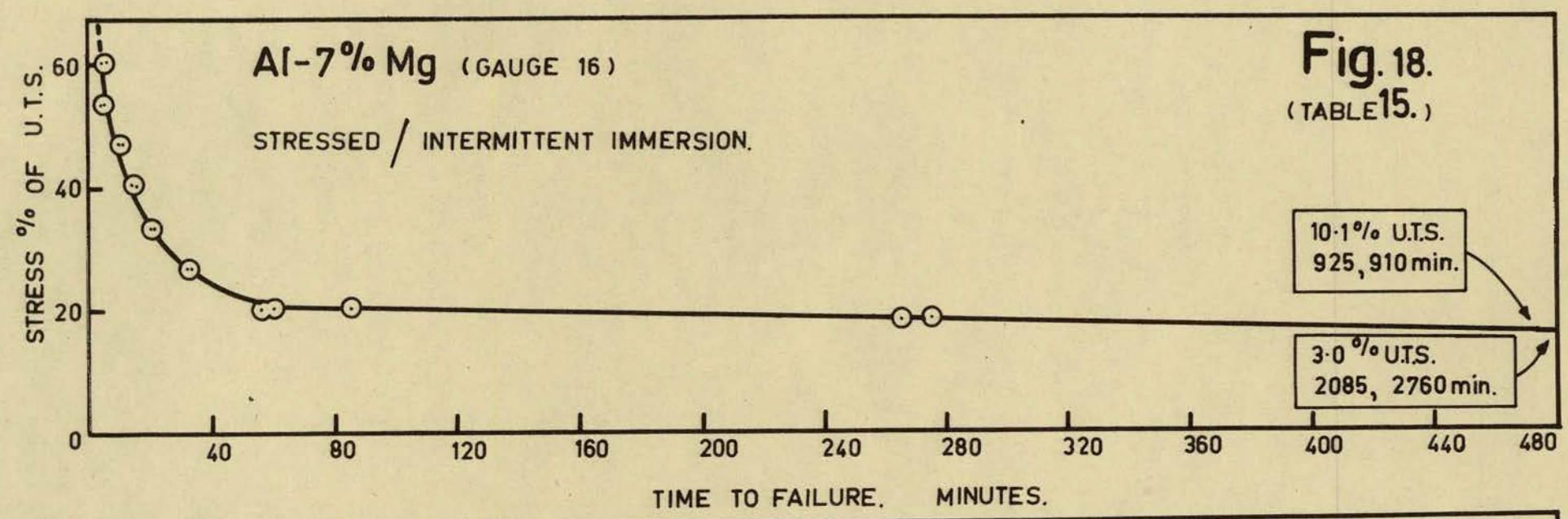


Fig. 18.
(TABLE 15.)

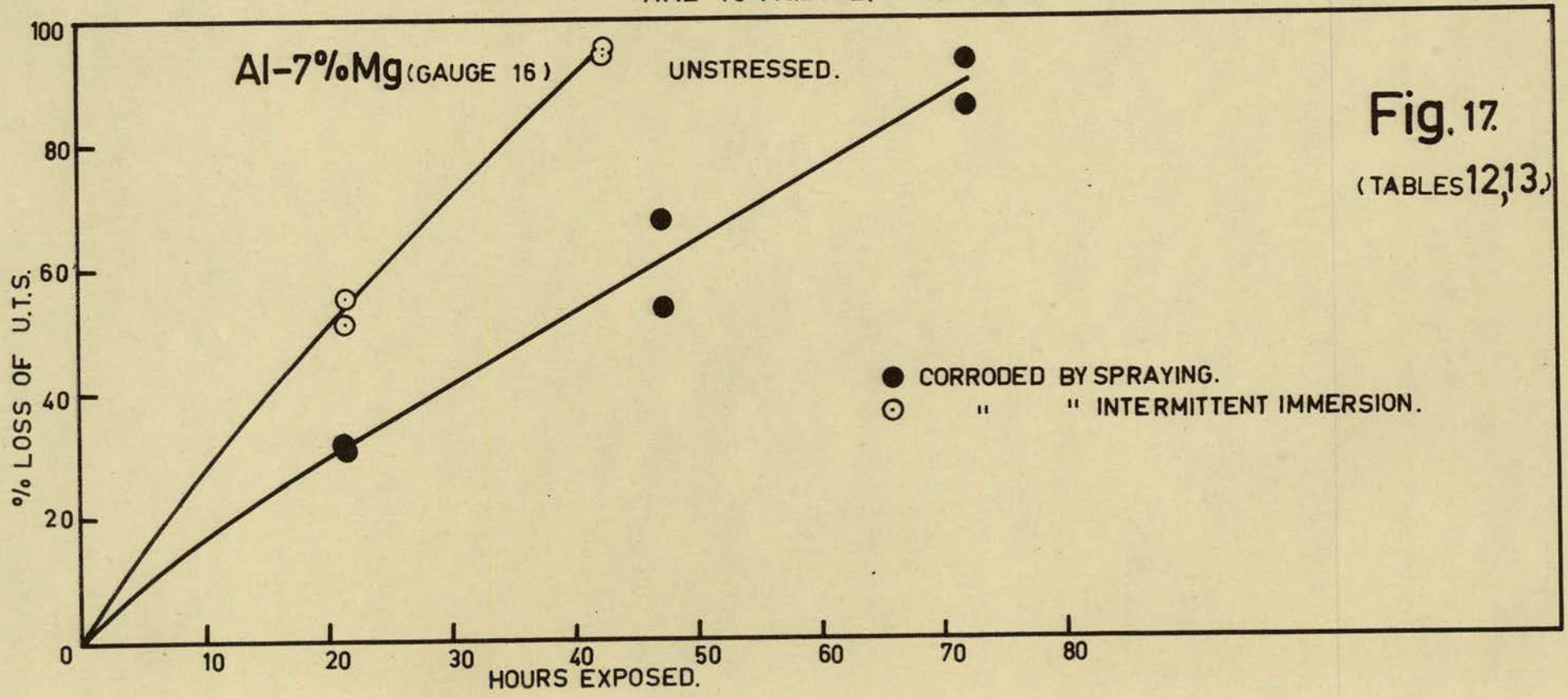


Fig. 17.
(TABLES 12, 13.)

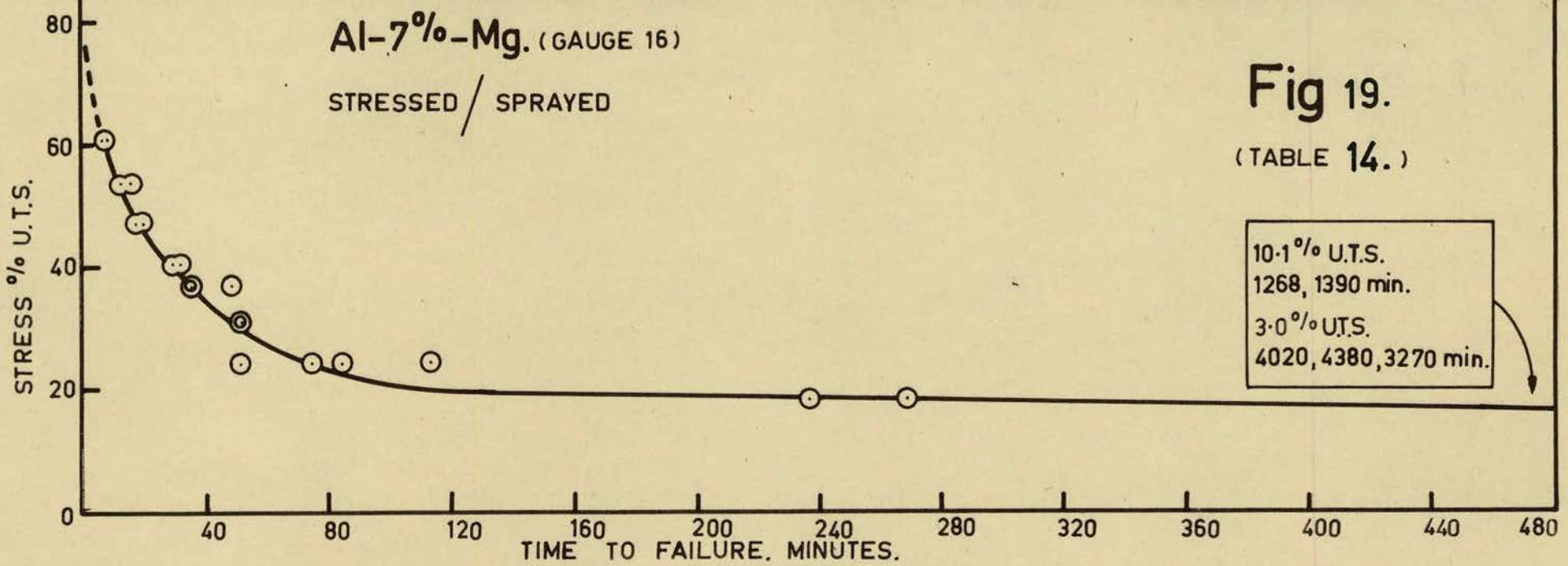


Fig 19.

(TABLE 14.)

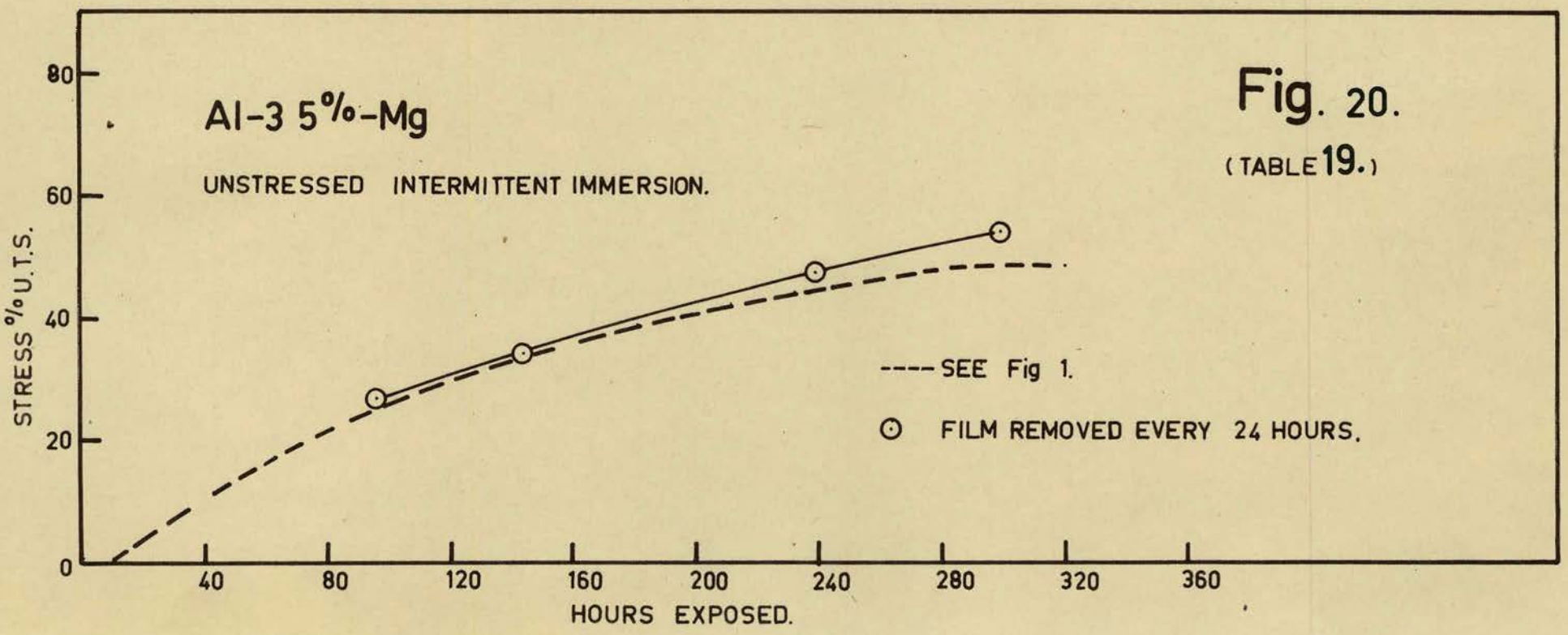


Fig. 20.

(TABLE 19.)

(b) Aluminium-7%-Magnesium.

The unstressed curves for both intermittent immersion and spray are shown in Fig. 17 (Tables 12, 13). The intermittent immersion curve shows loss of U.T.S. proceeding with time until the wire disintegrates or is broken by the movement of the cycling corrosive solution. Although the spray corroded wires did not disintegrate, loss of U.T.S. proceeded until the wires became too fragile to handle easily. It can be seen that the rate of loss of U.T.S. by intermittent immersion is three times as great as the loss by spraying.

The applied stress vs. time-to-failure curves are shown in Figs. 19, 18 (Tables 14, 15). Times to failure by spraying are considerably longer than those recorded by intermittent immersion at equivalent stresses.

The derivation of the stress-corrosion susceptibilities are shown in Figs. 21, 22 (Tables 16, 17). The values of 76% and 83% are reasonably comparable and also compare favourably with the value derived by Jones (3) for the same alloy. It can be seen that the curves have been extrapolated to pass through the origins. If minimal stress dS

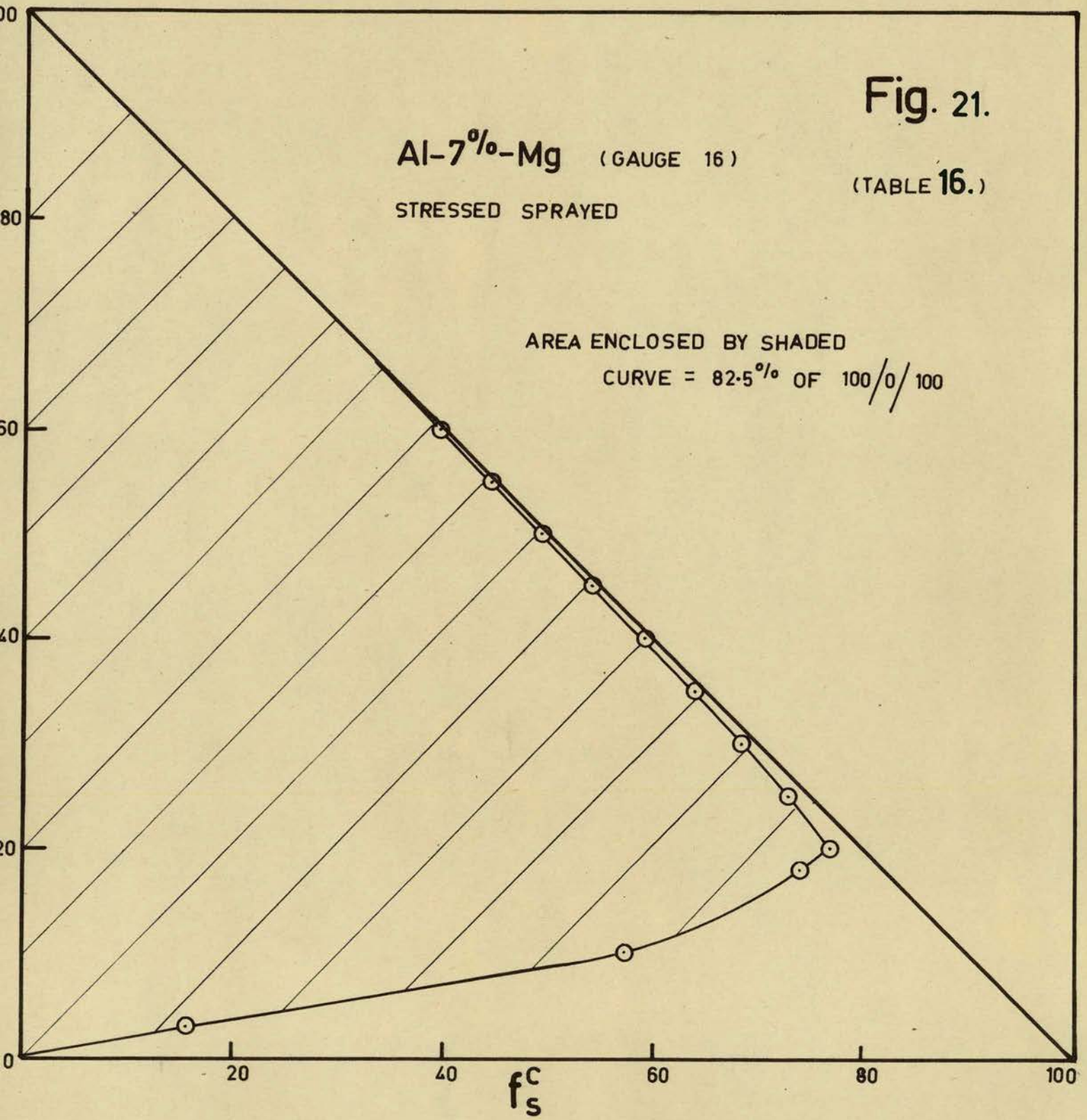


Fig. 21.
Al-7%-Mg (GAUGE 16)
STRESSED SPRAYED
(TABLE 16.)
AREA ENCLOSED BY SHADED
CURVE = 82·5% OF 100/0/100
00
80
60
40
20
0
20
40
60
80
100
f_s^c

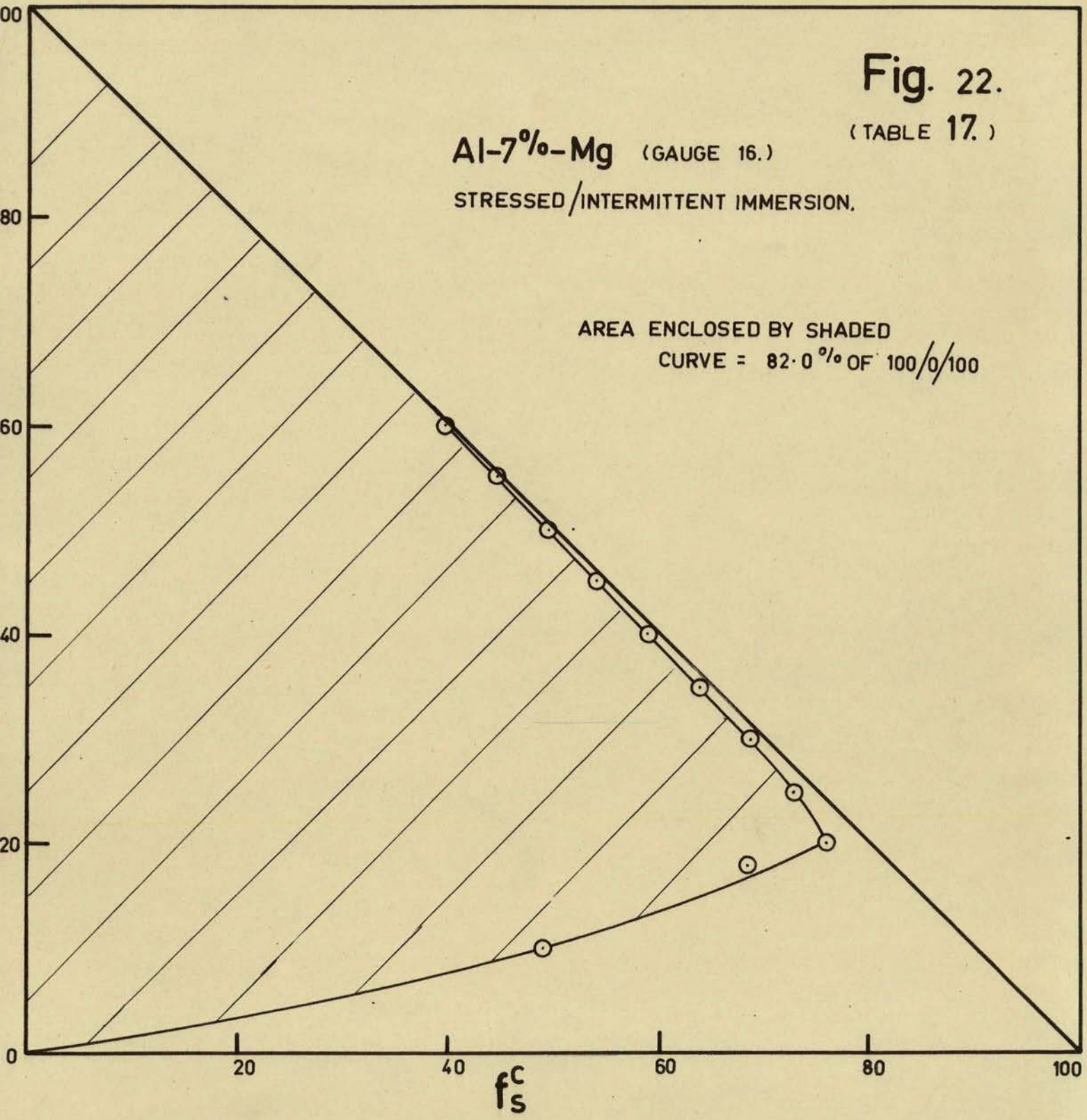


Fig. 22.
(TABLE 17.)
Al-7%-Mg (GAUGE 16.)
STRESSED/INTERMITTENT IMMERSION.
AREA ENCLOSED BY SHADED
CURVE = 82·0 % OF 100/0/100
00
80
60
40
20
0
20
40
60
80
100
f_s^c

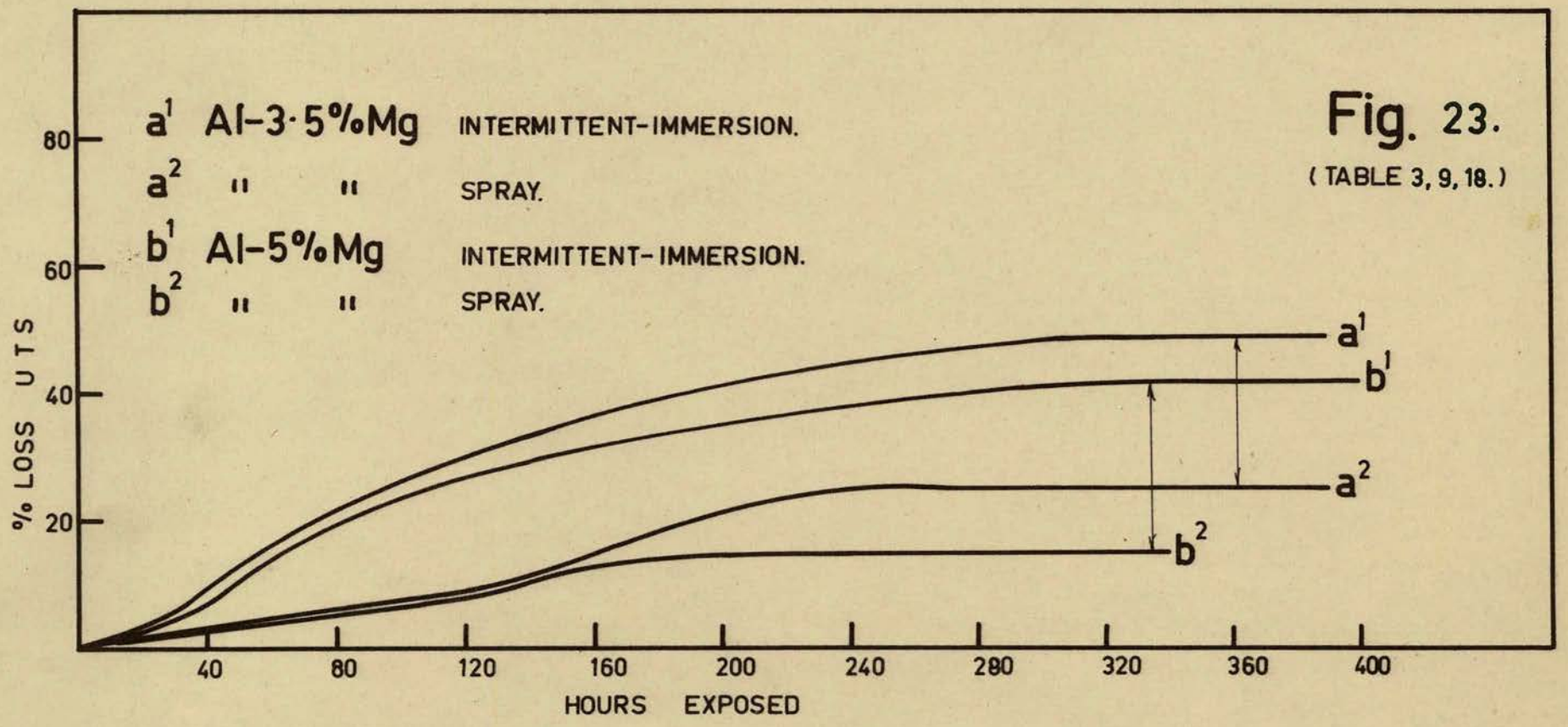


Fig. 23.

(TABLE 3, 9, 18.)

is applied and assuming that its effect on the corrosion pattern is very small, then failure i.e. 100% loss of U.T.S. will occur in 28 hours in the case of the specimen tested by intermittent immersion.

For minimal stress dS $S_s^c = 100 - dS \pm 100$

$S_u^c = 100$ ... at 28 hours.

and $f_s^c = 0$. i.e. the curve passes through the origin.

DISCUSSION. Part II.

DISCUSSION Part II. (See Experimental Part II.)

As stated previously the object of the work discussed in this section was primarily to compare stress-corrosion susceptibilities determined by the method of spraying with values obtained for the same alloys corroded by intermittent immersion.

The experimental work was carried out on part of the same sample of Al-3½%Mg wire used in Experimental Part I and also Al-7%Mg S.W.G. 16 wire which had been prepared along with rods of various other gauges from a single billet of the alloy as described in Experimental Part III. It was felt that these alloys were representative of the group under investigation but in view of the displacement with respect to the corresponding curve of Al-3½%Mg (Fig. 23) of the unstressed corrosion-time curve of the 5%Mg alloy obtained by Jones (2) it was decided for the purpose of comparison to reconstruct the latter curve using the method of spraying.

The unstressed corrosion-time curves of the 3½%Mg and 5%Mg alloys are shown in Figs. 14 and 23, Tables 9 and 18. In each case the rate of loss is less than that incurred by intermittent immersion. From Fig. 23 it can be seen that the curve of

Al-5%Mg again falls below that of the 3½%Mg alloy and that the differences in the respective asymptotes obtained by the two methods of corrosion are similar in terms of % loss of U.T.S. and in fact equal within the limits of experimental error. Since the laboratory pretreatments were identical it can only be supposed that some other factor either associated with the manufacture of the alloy or the fabrication of the wire is responsible for the unexpected difference in the asymptotes of the unstressed corrosion-time curves of the two alloys. It is suggested that the factor may be the rate of cooling during the commercial annealing process or the annealing temperature itself.

Fig. 17, Tables 12 and 13 show the unstressed corrosion-time curves of Al-7%Mg obtained by intermittent immersion and spraying. Here again the rate of loss of U.T.S. is considerably less by spraying than by intermittent immersion. As far as oxygen requirement is concerned the method of spraying would be expected to have the advantage since the gaseous transfer through the film of corrosive solution is not interrupted and discontinued for half the time of the test as it is in the case of intermittent immersion. If on the other hand

the oxygen available is greatly in excess of requirement during corrosion by both methods, and this seems probable since corrosion takes place although to a less extent during total immersion, then some other factor which is not common to both methods must be responsible for the difference in corrosion rates. One outstanding difference between the two methods lies in the degree of physical disturbance which accompanies contact with the corrosive solution. The up and down passage of corrosive solution during intermittent immersion results in a scouring effect which is entirely absent in the case of spray testing. It is suggested that the removal of corrosion products from the surface of attack which results from this liquid scouring is probably responsible for the higher rate of loss of U.T.S. which is incurred during corrosion by intermittent immersion.

The applied stress vs. time-to-failure curves for Al-3½%Mg and Al-7%Mg are shown in Figs. 15 and 19, Tables 10 and 14. The corresponding curve obtained by intermittent immersion of Al-7%Mg is shown in Fig. 18, Table 15. The applied stress vs. time-to-failure curve of the 3½%Mg alloy obtained by intermittent immersion is that

previously described in Experimental Part I and shown in Fig. 2, Table 4. The observed times-to-failure of the 7% Mg alloy were very short, more than half being less than one hour. The time axes of the curves are therefore shown in minutes and not hours as in the other curves. It can be seen that the stressed curves for both alloys are shallower in the case of spray testing. Times-to-failure by intermittent immersion were clearly much shorter than those obtained by spraying and it is evident that intermittent immersion is the more severe accelerated corrosion treatment. This being so it might be expected that a difference would be observed in the threshold stresses obtained by the different methods of testing. No such difference was observed. The results in fact suggest that although times-to-failure for the same stresses may vary according to which of the two methods is used, the threshold stress is, within the limits of the two methods described, independent of the method. Stress-corrosion susceptibilities of Al-3½%Mg and Al-7%Mg as determined by the method of spraying are shown in Figs. 16, 21, Tables 11 and 16, and may be compared with those obtained by intermittent immersion, Figs. 4, 22, and Tables 5, 17. The

susceptibilities of the 3½%Mg alloy were 18.5 and 18.4 and for the 7%Mg alloy 82 and 82.5, the latter comparing favourably with the value of 79 obtained by Jones (3). In this close agreement between the different methods of testing is seen ample justification for the insistence of Dix (34) and Champion (105) that specimen blanks must be exposed to the corrosive solution without, as well as with, the application of stress in order to obtain a true assessment of the effect of applied stress on the corrosion of metals and alloys.

It is of interest that the value of f_s^c in the case of Al-7%Mg corroded by intermittent immersion at an applied stress of 3% U.T.S. is near zero. This suggests that an applied stress of or below this value has little effect on the pattern of corrosion and adds weight to the reasoning previously offered for extrapolating the stress-corrosion susceptibility curve to the origin for an alloy whose unstressed corrosion-time curve does not become asymptotic to the time axis. The loss of strength of such an alloy when corroded unstressed approaches the U.T.S. before film formation has proceeded far enough to reduce the rate of loss by stifling. This is probably due to

a very high rate of intergranular penetration compared with the rate of film build-up or to a third factor such as film rupture caused by the breaking up of the corroding surface by deep-seated corrosion products of large bulk. (See Al-7%Mg, gauge 0, shown in Fig. 49.)

Probably the chief difficulty which has to be overcome before reproducible results can be obtained by the spray method of testing is the prevention of concentration or dilution of the corrosive liquid film on the specimen under test. It can be seen from Fig. 46e that errors of the order of -10 to +100% in the stress-corrosion life of Al/Mg tested with 3% NaCl solution can result from a $\pm$1% change in the chloride concentration of the corrosive solution. This change of concentration is due either to condensation or evaporation of water into or from the corrosive solution film and is dependent on the relative humidity of the immediate atmospheric environment which is in turn a function of temperature. The main purpose of the spray cabinet is therefore to maintain constant the temperature and humidity of the air which it encloses so that films of corrosive solution adhering to the test-pieces remain unchanged (except for chemical changes due to

corrosion) during the entire period of exposure of the test-pieces. Accelerated corrosion testing of a quantitative nature is usually carried out in this country at 25°C (77°F.) which is often considerably above ambient temperatures especially in the cold season. To offset this, spray cabinet designs normally include a system of auxiliary heating. Point heat sources must be avoided since they give rise to steep temperature gradients within the cabinet and these result in the formation of convection currents which in turn give rise to overall non-uniform conditions of humidity. Low temperature heaters of high capacity are in order and it was with this in mind that the cabinet shown in Fig. 13 was designed. As can be seen the entire floor of the cabinet consists of the upper surface of the heater and largely overcomes the problem of convection currents due to disproportionate temperature gradients. The humidity within the cabinet was further stabilised by maintaining within it a large shallow dish of corrosive solution. The vapour pressure of the solution was the same as that of the moist film on the test-pieces and produced suitable conditions of humidity when placed within

the cabinet some hours before testing began. Absolute control of humidity within a small volume (ca. 1 ft^3) which has to be exposed periodically to the outside atmosphere is not a simple matter and the most that can be done without the use of overelaborate apparatus is to provide sufficient control to give reproducibility of results. Perryman and Hadden (103) have shown that at high relative humidities when stressed specimens remain wet they tend to fail more rapidly than when the corrosive solution film is allowed to dry off. They also showed that a change in the relative humidity from 71% to 81% resulted in a decrease in the stress-corrosion life of Al-10%Mg by a factor of 3 and that few failures occurred when a relative humidity of 100% was maintained. The dependence of results obtained by spray testing on such a critical variable as humidity complicates comparison of the method with intermittent immersion and total immersion. Champion (104) states "as a general rough guide" that intermittent immersion and spraying are comparable and that both are more severe than total immersion. Perryman and Hadden (103) have produced some

evidence to show with respect to Al-10%Mg stressed in the form of bent loops that spraying is more severe than total immersion. In view of this evidence and in the light of the work described in this thesis it is suggested that the probable order of increasing severity is (1) total immersion, (2) spraying and (3) intermittent immersion. The position of spraying in the series is however subject to the limits of the conditions described in Experimental Part II.

EXPERIMENTAL PART III.

EXPERIMENTAL Part III.

THE EFFECT OF CROSS-SECTION ON THE STRESS-CORROSION SUSCEPTIBILITY OF ALUMINIUM-7%-MAGNESIUM RODS.

Materials and preparation of test-pieces.

The investigation of the effect of cross-section on the stress-corrosion susceptibility of aluminium-magnesium alloys was carried out on Al-7%Mg on account of its higher degree of reproducibility of test results and because its higher rate of unstressed loss of U.T.S. and shorter times to failure were a decided advantage in what could easily have turned out to be a rather overlong programme.

From a specially cast billet of Al-7%Mg, rods and wire were rolled and drawn into 100 foot lengths of S.W.G.s 0, 4, 8, 10, and 16 by Messrs. James Booth, Birmingham. The pieces were then cut to 6 foot lengths and commercially annealed in one operation. In this "as received" condition the alloy was delivered to the laboratory where the lengths were cut to 3 feet and linearly overstrained 10% by means of an Olsen wire testing machine. The test-pieces were cleaned and degreased with 10% nitric acid and water as before, wiped with filter

paper and aged at 125°C for 24 hours. After ageing, each piece was cut to 16 inches and threaded at each end, the threaded portion being $\frac{3}{4}$inch long. B.S.W. dies were used for gauges 0 and 4 and B.A. dies for gauges 8 and 10. The gauge 16 wires were not threaded since it was intended in this case to apply stress by means of weighted steel-yards. All test-pieces were resin coated as before so that a 7 inch middle length remained exposed. During the resin dipping the threaded ends of the rods were protected with cellotape. Chemical analyses and average mechanical properties of representative specimens of each gauge are shown in Tables 20 and 21.

Apparatus.

For gauges other than 16 S.W.G. breaking stresses per cross-section ranged from 634 lb to 4120 lb and it was apparent that the installed system of weighted steel-yards was inadequate to handle loads of this order. The problem could not be overcome simply by increasing the strength of the steel-yards since dead weights of the order of 500 lb and localised tensions of 2000 lb and upwards could not be accommodated by the existing apparatus. It was decided, therefore, to make use of coiled springs

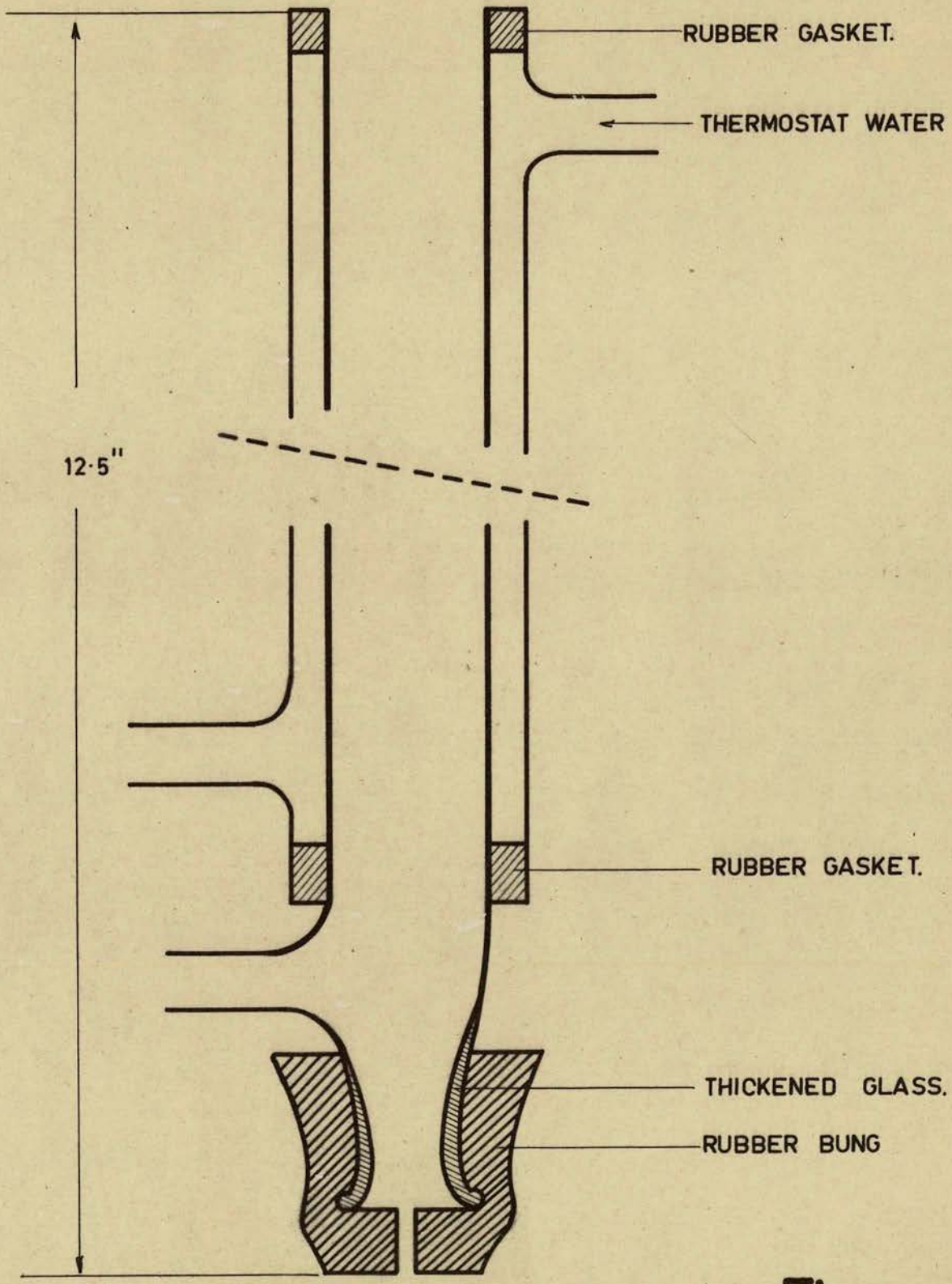
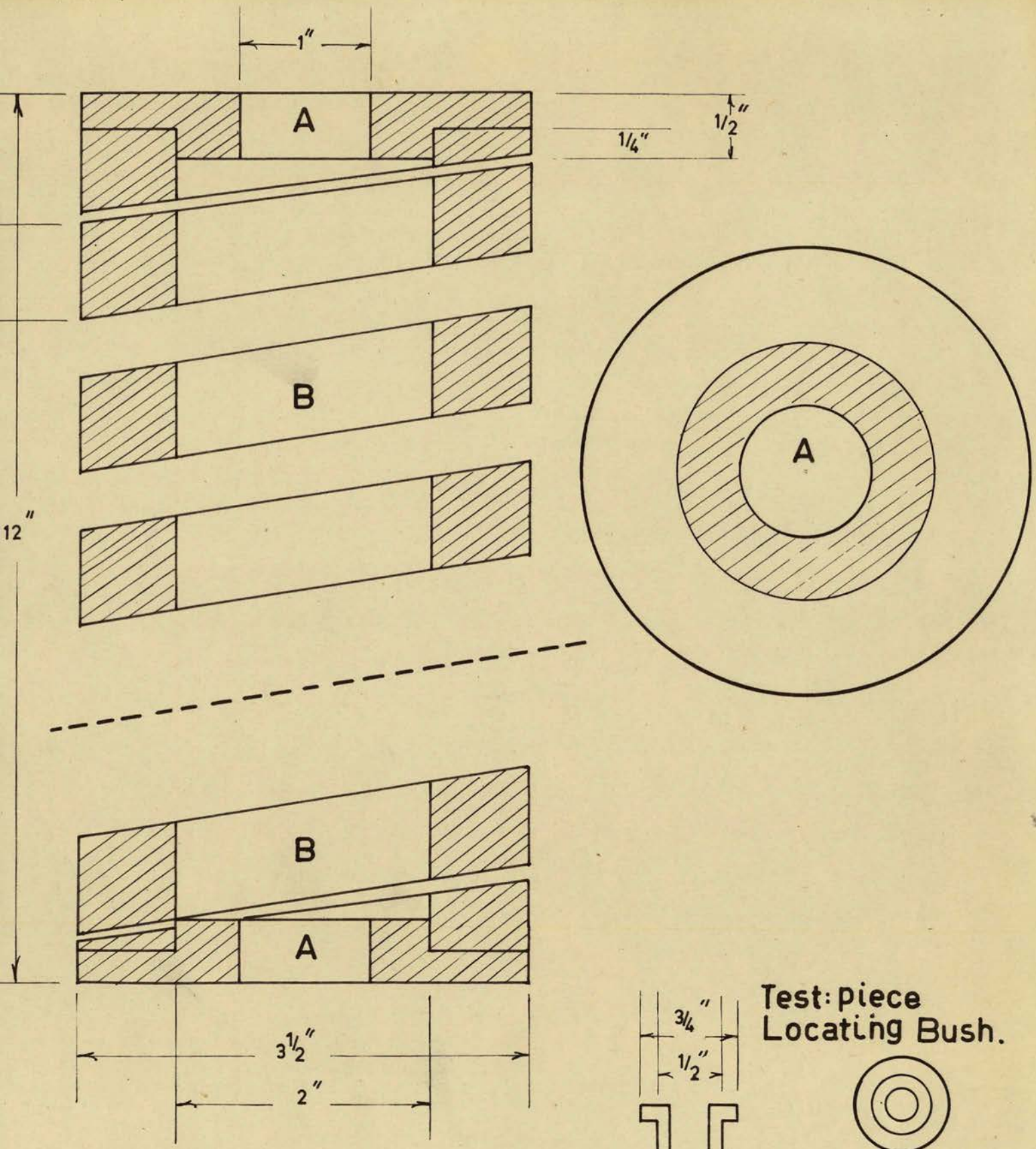


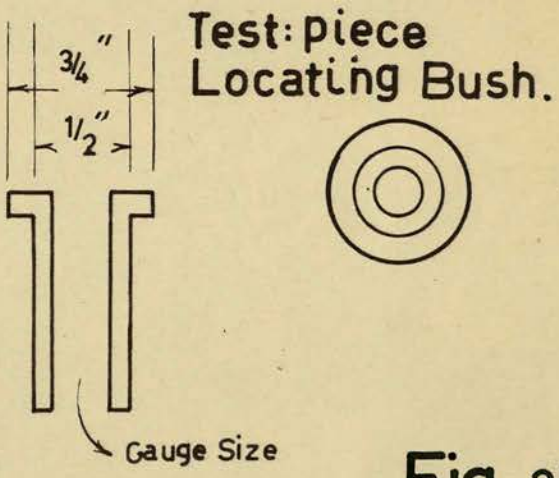
Fig. 24.

Corrosive Solution Tube. (TO SCALE)

to obtain the desired tensile stresses and the unit described by Loose and Barbian (6), with certain modifications, appeared likely to meet the requirements of high applied tensile stress without increase in overall dead weight. From the determined 0.1% proof stresses of the various gauges of the strain-aged alloy, working applied stresses were calculated and, based on these calculations, an order was placed with The Cockburn Engineering Company, Cardonald, Glasgow, for four coil compression springs of linear load factors 2000, 1000, 500, and 300 lb./inch. Overall lengths and outside coil diameters were specified and it was requested that the finished springs be cadmium plated to minimise rusting. On arrival at the laboratory the springs were load tested on a 10 ton Buckton tensile machine and the determined load factors were 2250, 1109, 529 and 317 lb./inch.

It was decided that each spring should be incorporated in an independent unit comprising a steel frame 15 x 4 inches (internal) with a draw-bar running through one end, the spring being compressed over the draw-bar to give the required tension between the draw-bar collar and the opposite end of the frame. Each unit should be suspended by two





Test: piece
Locating Bush.

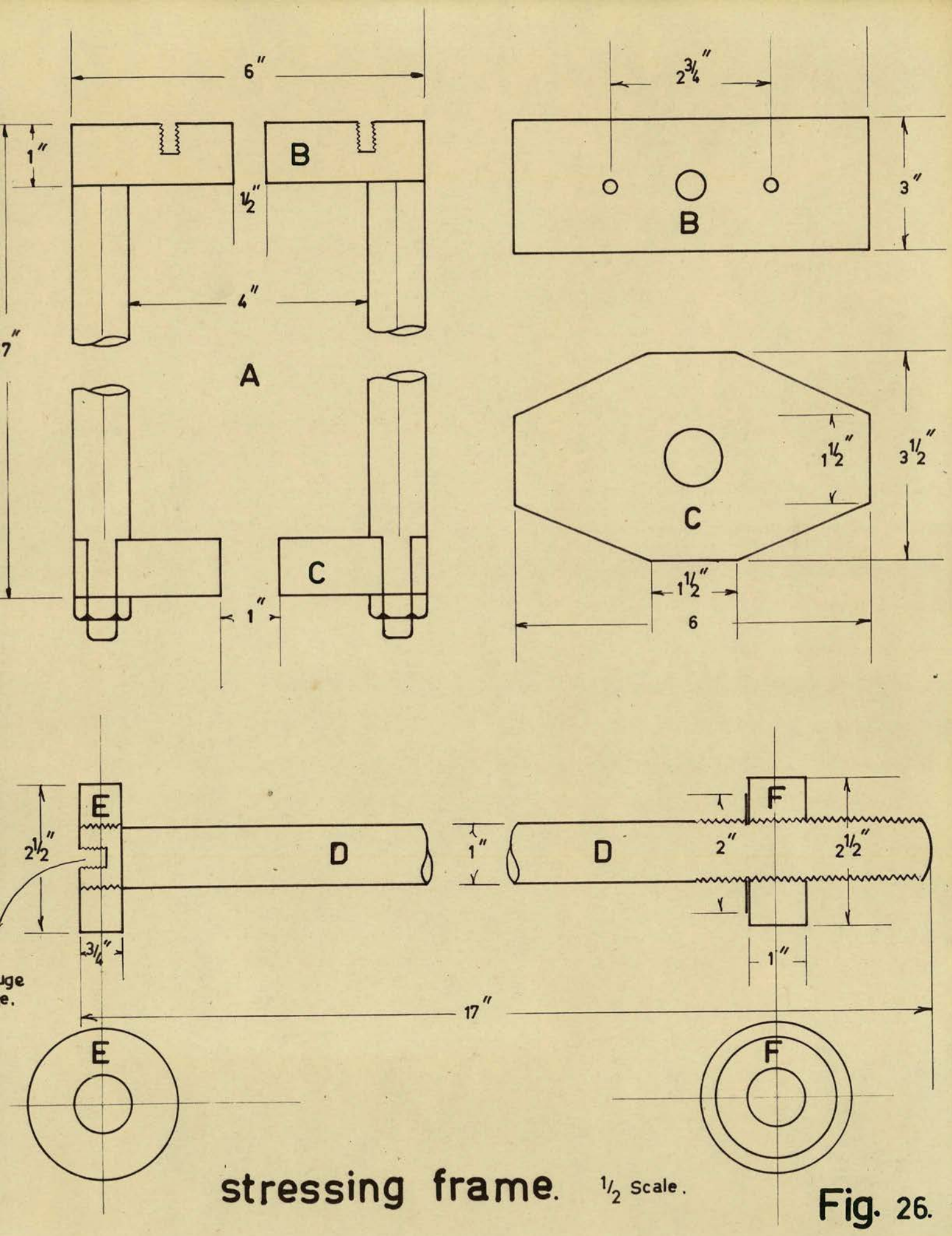
spring & end plates.

To Scale. B. (2000 lb/in.)

Fig. 25.

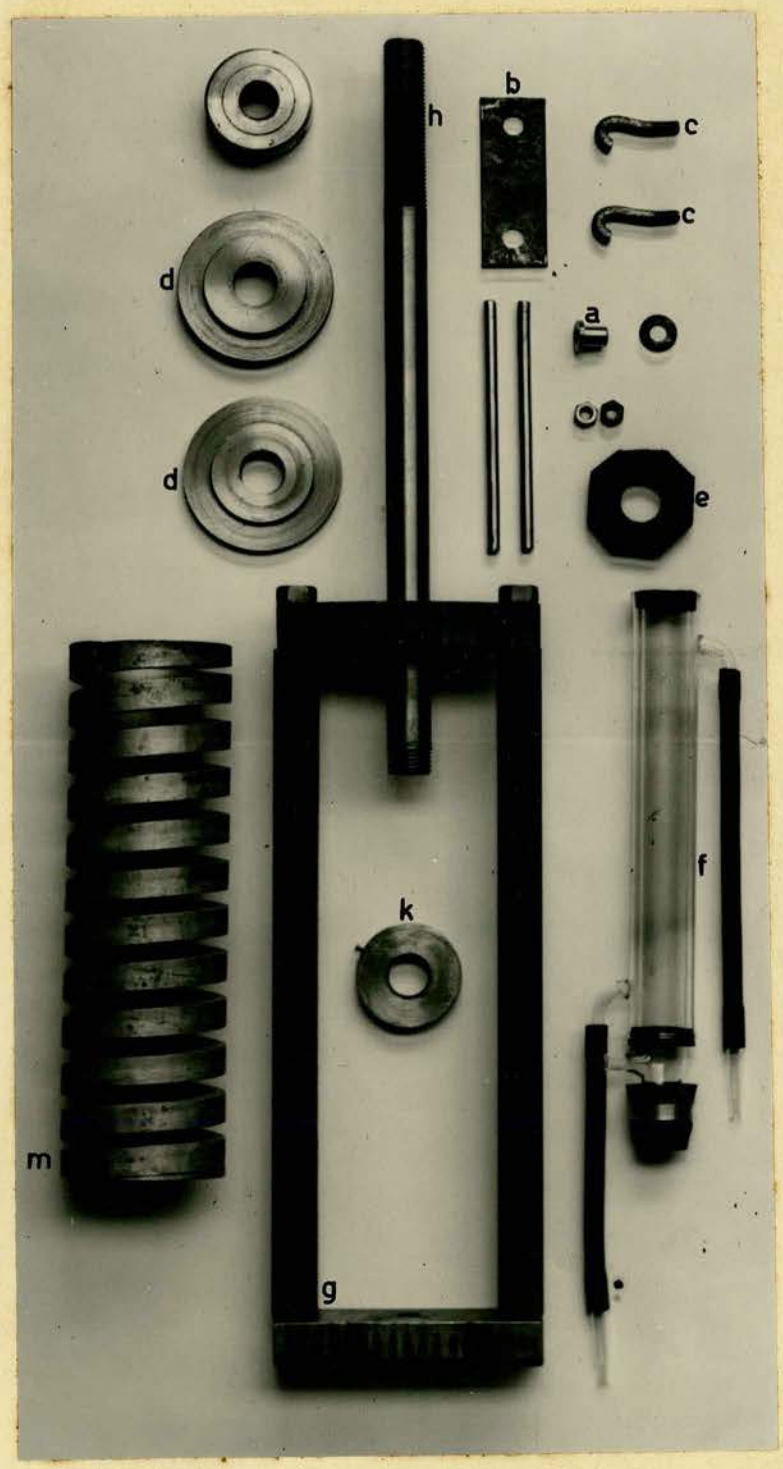
coil springs from the upper beams of the intermittent immersion apparatus from which the steel-yards had been removed. The two point suspension would prevent the shock of failure from being transmitted to the other operating units. (Fig. 28.)

The frame uprights were made from 1 inch hexagon bar and the top and bottom plates were cut to finished size from 1 inch plate by means of a profile burner. The bottom plate was drilled to take a 17 x 1 inch draw-bar which was keyed to the plate to prevent twisting of the test-piece while the spring was being compressed. The inside end of the draw-bar was drilled and tapped to take the threaded end of the test-pieces and was flush fitted with a screw collar $2\frac{1}{2}$ x $\frac{3}{4}$ inches as shown in Figs. 26 and 27. Half inch sponge rubber washers were fitted between the collar and the plate to absorb the shock of failure. The lower end of the draw-bar was threaded with a B.S.W. thread of 10 threads to the inch and fitted with a screw collar holed for tommy-bars. The spring ends were fitted with inset end plates which located the pull of the draw-bar as shown in Fig. 26. The top frame plates were holed to take a series of brass bushes drilled to accommodate the various gauges of test-pieces;



stressing frame. ½ Scale.

Fig. 26.



a SPECIMEN LOCATING BUSH.

b ARREST PLATE.

c SUSPENSION HOOKS.

d SPRING END PLATES.

e RUBBER SHOCK ABSORBER.

f CORROSIVE SOLN TUBE.

g FRAME.

h DRAWBAR.

k DRAWBAR COLLAR.

m SPRING 1000 L B

SPRING STRESSING UNIT.

Fig. 27.

these served to locate the test-pieces. The upper threaded portion of the test-piece projected through the top plate and was anchored by two steel nuts. (Fig. 28) The glass corrosive solution tube was modified as shown in Fig. 24. The rubber sleeve on the bottom of the tube was cemented with polymethacrylic resin and wired firmly to withstand the sudden jerk at failure and the top of the tube was positioned on the test-piece by means of a loose fitting rubber bung.

Method of Testing.

To assemble the frame, the draw-bar was passed through the keyed hole in the bottom plate and the upper screw collar fitted. The top end plate, spring, bottom end plate and bottom screw collar were fitted over the draw-bar in the order stated. The test-piece was passed through the rubber sleeve of the corrosive solution tube so that some two inches projected from the bottom. The tube and test-piece were then fitted into the frame by passing the upper end of the test-piece through the top plate before screwing the lower end into the upper end of the draw-bar. The whole unit was inverted and held firmly in a jig while the spring

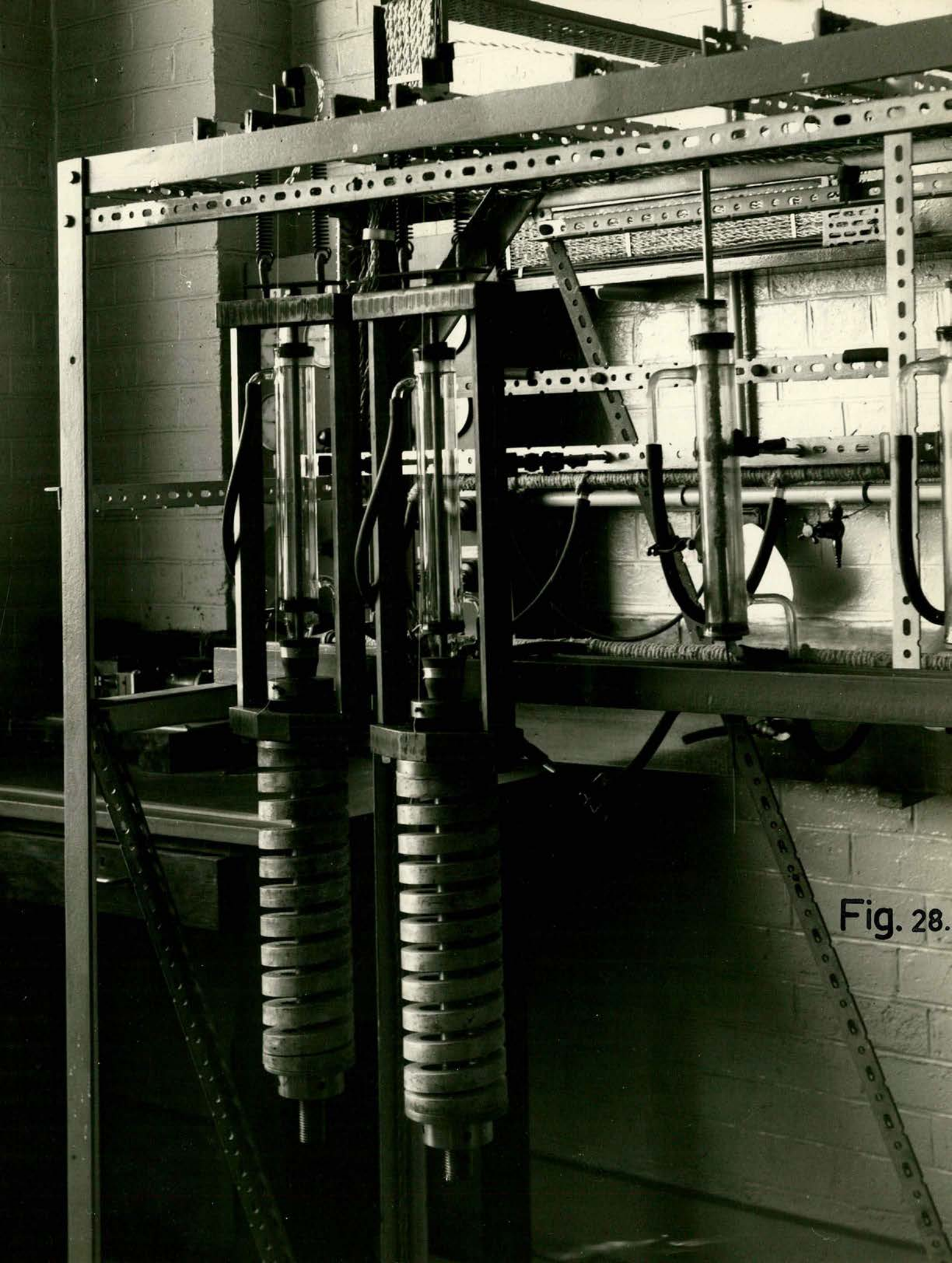


Fig. 28.

was compressed to give the required tension. The unit at this stage was quite rigid and could be handled easily. Screw hooks were passed through an arrest plate and screwed into the top of the upper frame plate. The completed unit was suspended from light coil springs by means of the hooks as shown in Fig. 28. The arrest plate prevented the upper half of the test-piece from flying out of the tube at failure.

Thermostat and corrosive solution tubes were connected up and the overhead time switch attached to the upper draw-bar collar by a length of stout thread. At failure the movement of the draw-bar was less than $\frac{1}{2}$ inch and this was quite sufficient to operate the time switch.

The corrosive solution was 3% sodium chloride buffered to pH 6 with sodium acetate and acetic acid and the immersion cycle remained unchanged at 2 minutes. During the testing of the heavier gauge specimens it was observed that the activity of the corrosive solution decreased markedly after a period of about 7 days with the result that unstressed losses were considerably less than those obtained with freshly prepared solution. A gelatinous suspension of what appeared to be MgOH and/or $Al(OH)_3$ appeared in the solution after 3 days and, since it

was believed that this was associated with the loss of activity observed, the corrosive solution was changed every 3-4 days. This was in marked contrast to the behaviour of the corrosive solution during the testing of the S.W.G. 16 alloys when activity was preserved for upwards of 28 days. It is almost certain that the active life of the corrosive solution is a function of the ratio of the alloy exposed to the volume of circulating solution. Fig. 49 shows how after 72 hours the heavier gauge alloy rods split and flaked. This resulted in a very large increase in exposed surface. This phenomenon was not observed in the case of the 2½%Mg and 3½%Mg alloys and only to the extent of flaking in the S.W.G. 16 7%Mg alloy.

Unstressed test-pieces were subjected to intermittent immersion in the corrosive solution tubes of the original apparatus. See Experimental Part I.

Experimental Results.

Unstressed and stressed corrosion-time curves and derived stress-corrosion susceptibility curves are shown as follows:-

Gauge.	Figs.	Tables.
0.	29, 37, 39.	22, 27, 32.
4.	30, 38, 40.	23, 28, 33.
8.	31, 32, 41.	24, 29, 34.
10.	33, 34, 42.	25, 30, 35.
16.	35, 36, 43.	26, 31, 36.

Reproduction of unstressed corrosion-time results was satisfactory with the exception of those obtained with the S.W.G. 8 alloy in respect of which the spread of results was unexpectedly high. The explanation appeared to lie in the existence of a latent bend in the gauge 8 test-pieces which persisted in spite of the strain-ageing treatment. When the unstressed loss of U.T.S. reached approximately 40% the test-piece became bowed with the result that the corrosive attack was no longer evenly distributed. Cross-sections showed displacement of the unattacked core which was normally concentric with the long axis. With the heavier gauges of alloys it quickly became apparent that reproducibility depended critically on the vertical location of the test-piece, deviation of a few degrees from true vertical resulting in a low loss of strength being recorded.

Fig. 49 shows the appearance of unstressed

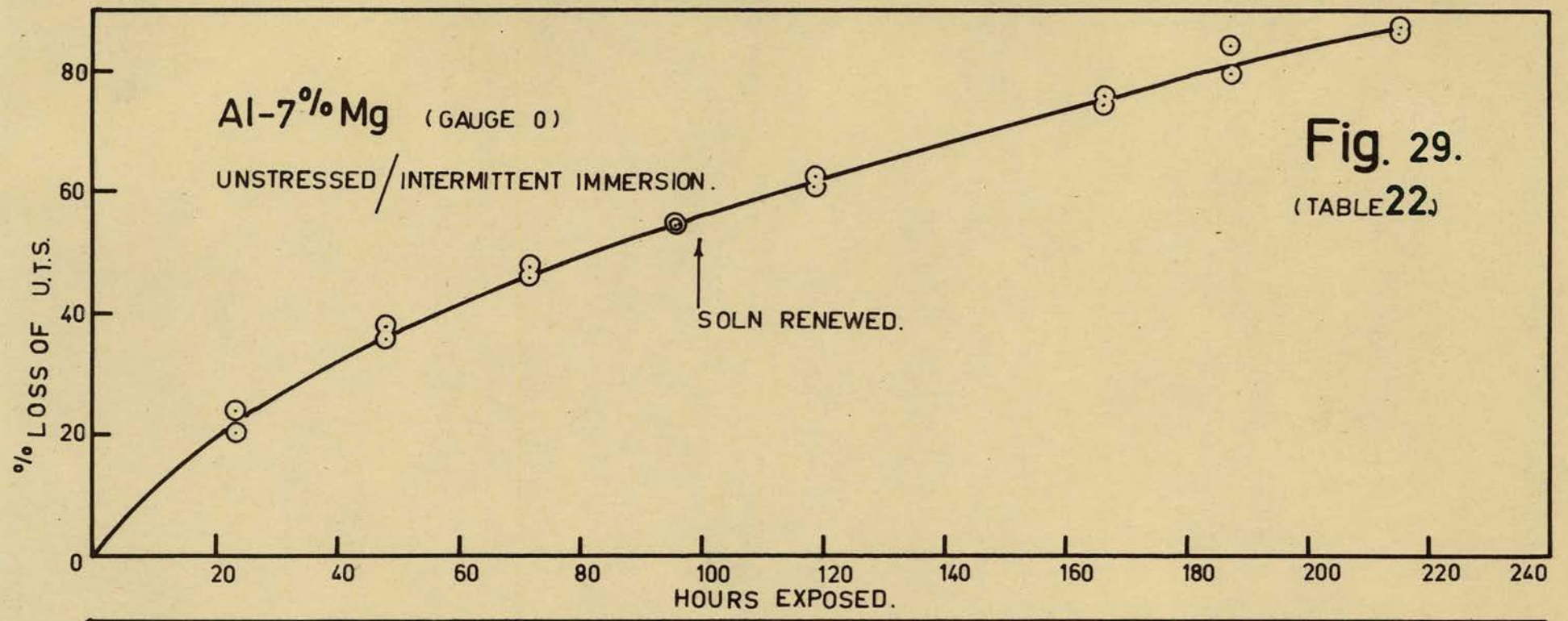


Fig. 29.
(TABLE 22.)

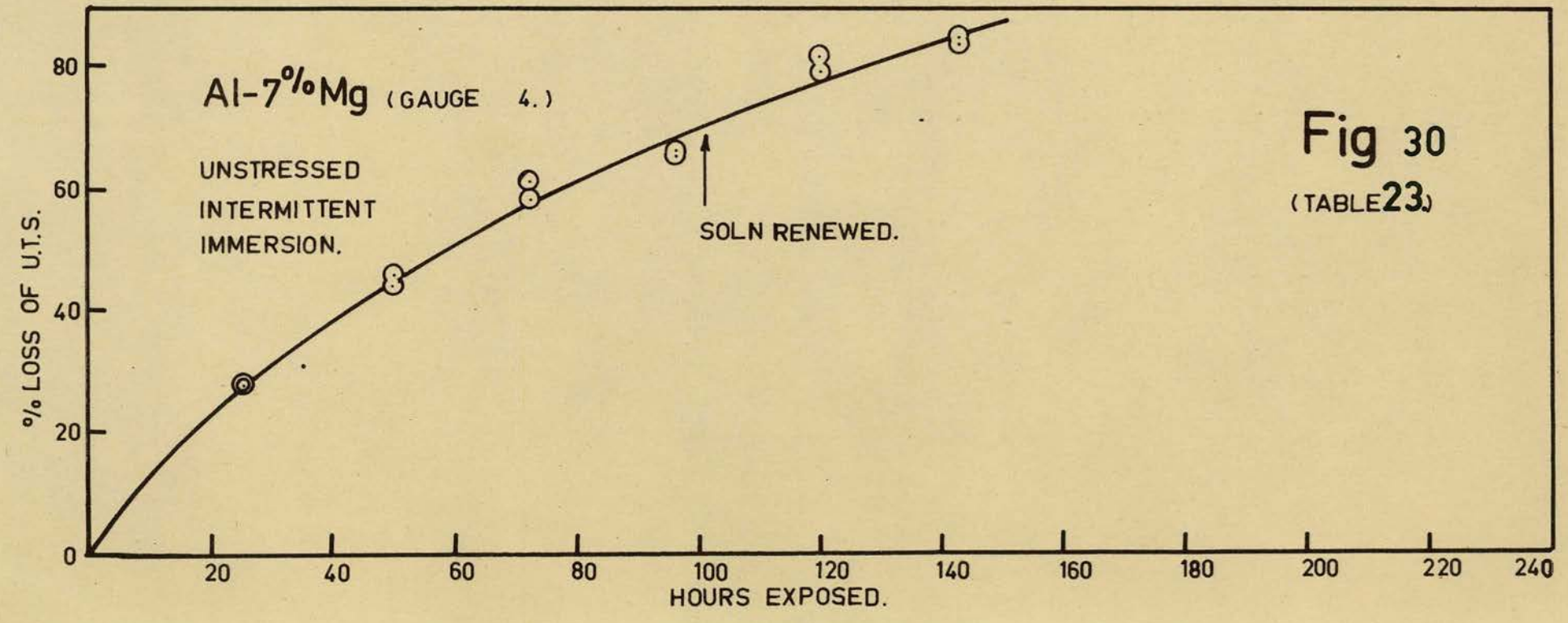


Fig 30
(TABLE 23.)

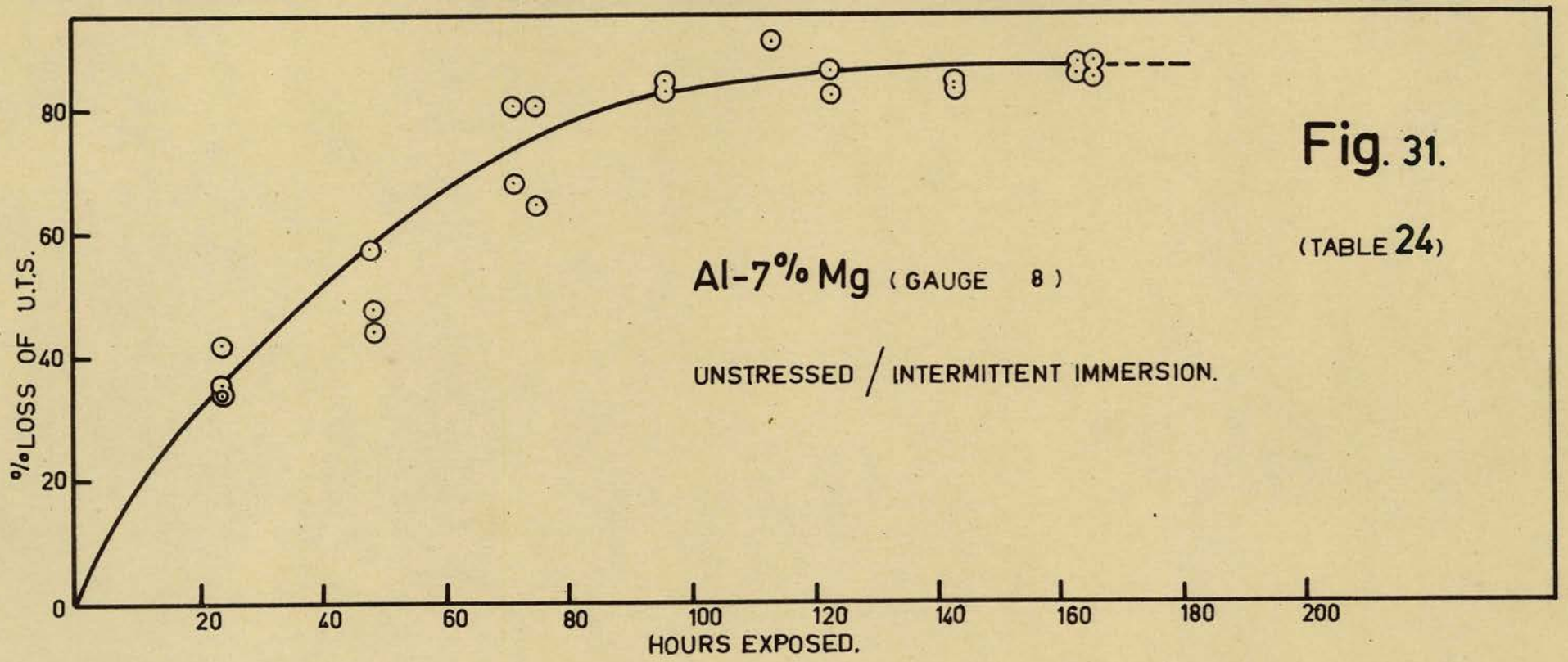


Fig. 31.

(TABLE 24)

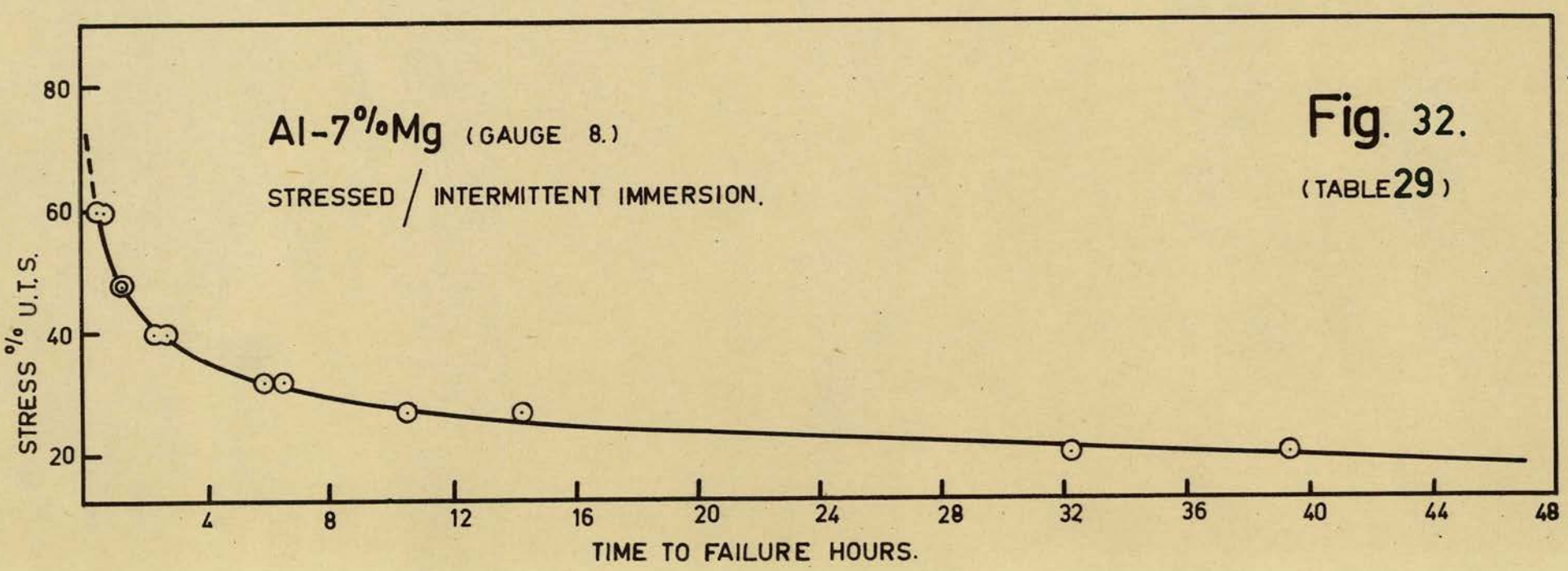


Fig. 32.

(TABLE 29)

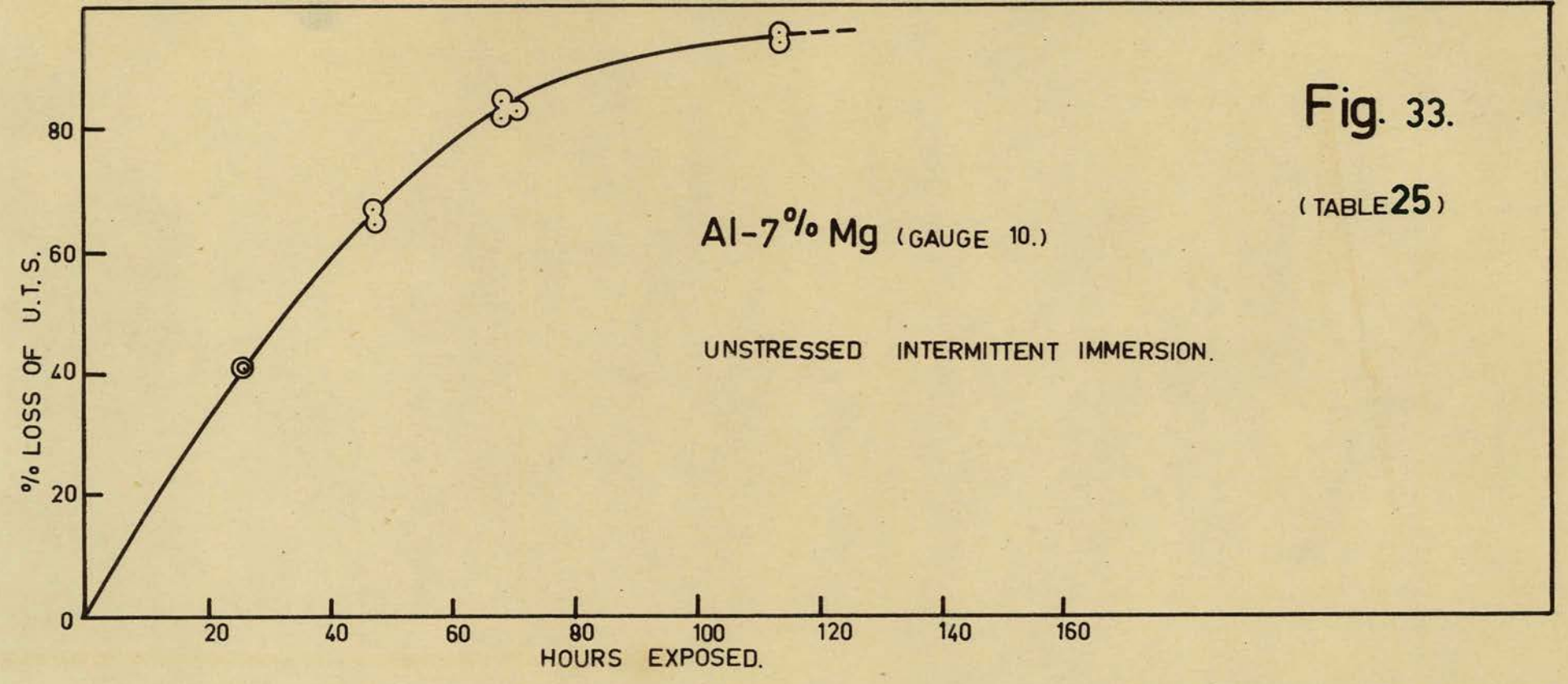


Fig. 33.

(TABLE 25)

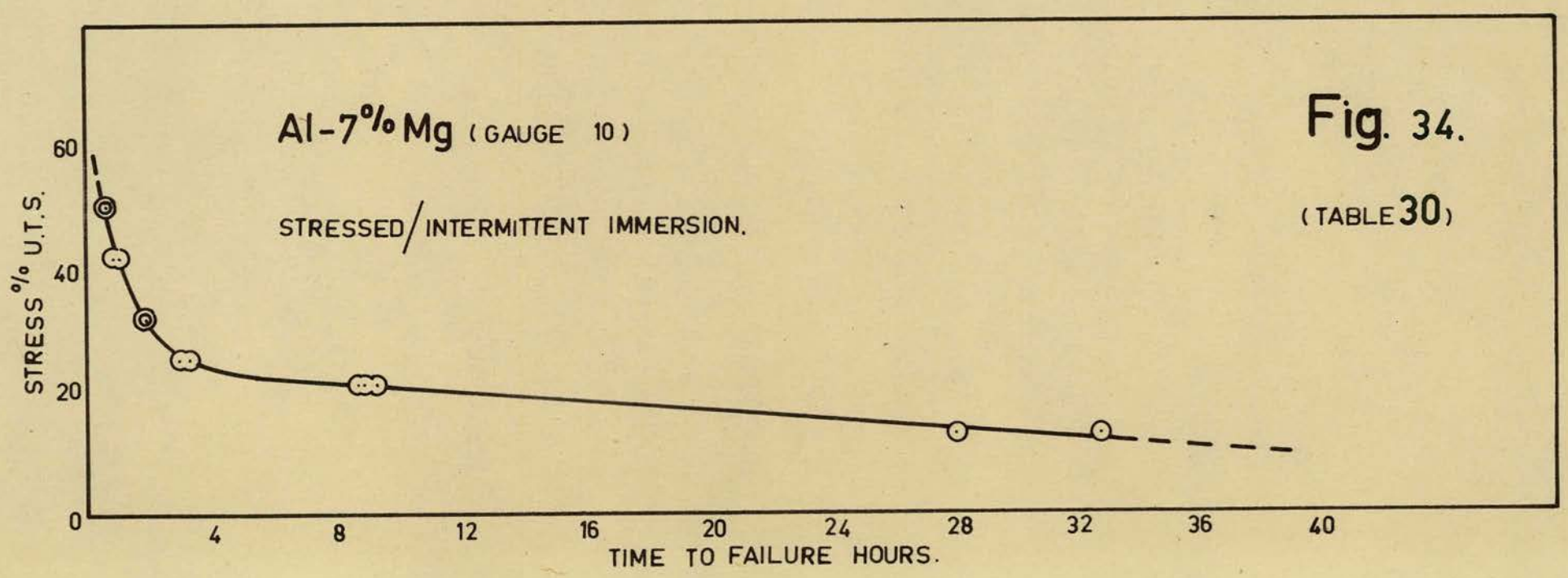


Fig. 34.

(TABLE 30)

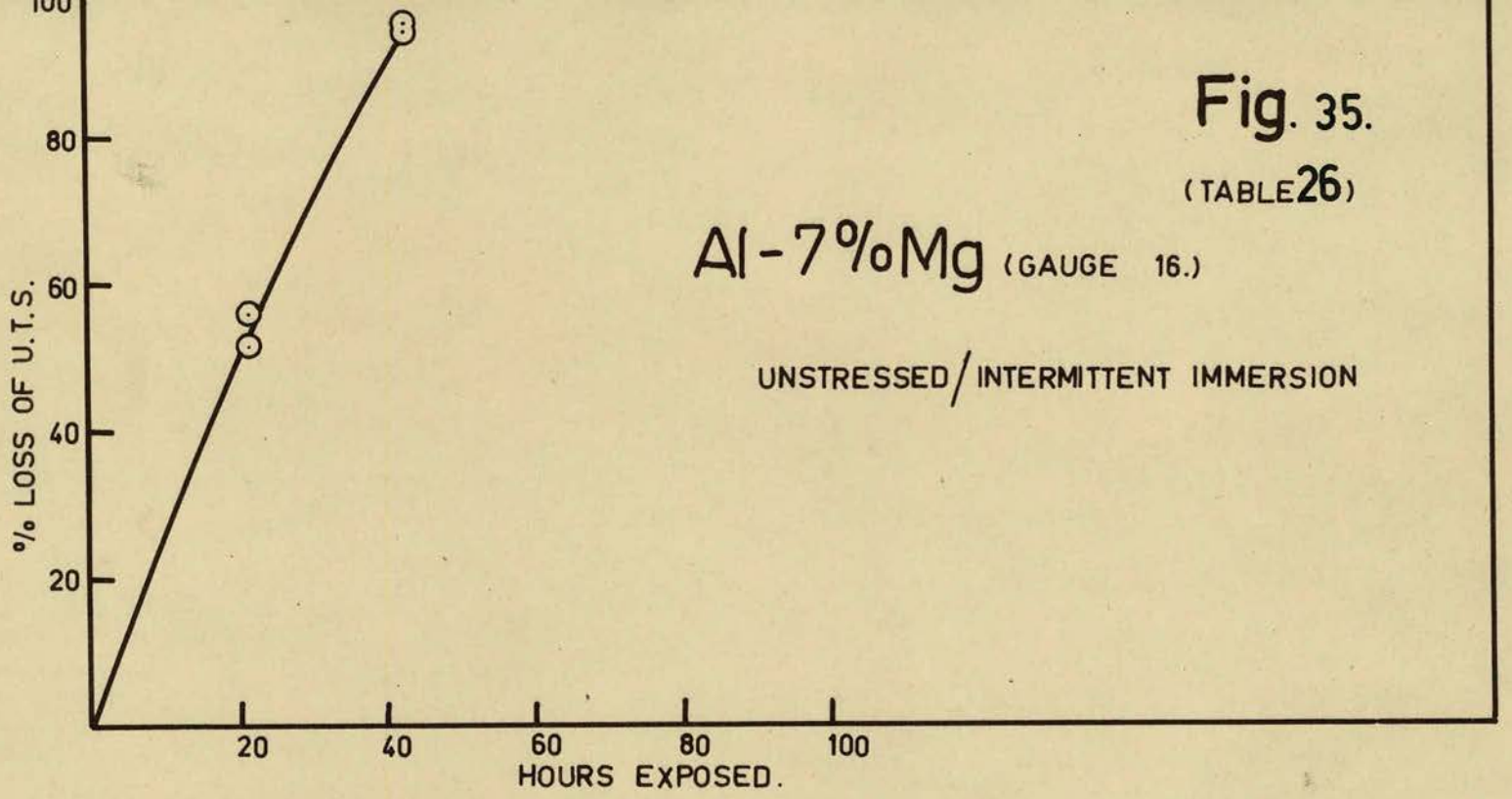


Fig. 35.

(TABLE 26)

Al-7%Mg (GAUGE 16.)

UNSTRESSED/INTERMITTENT IMMERSION

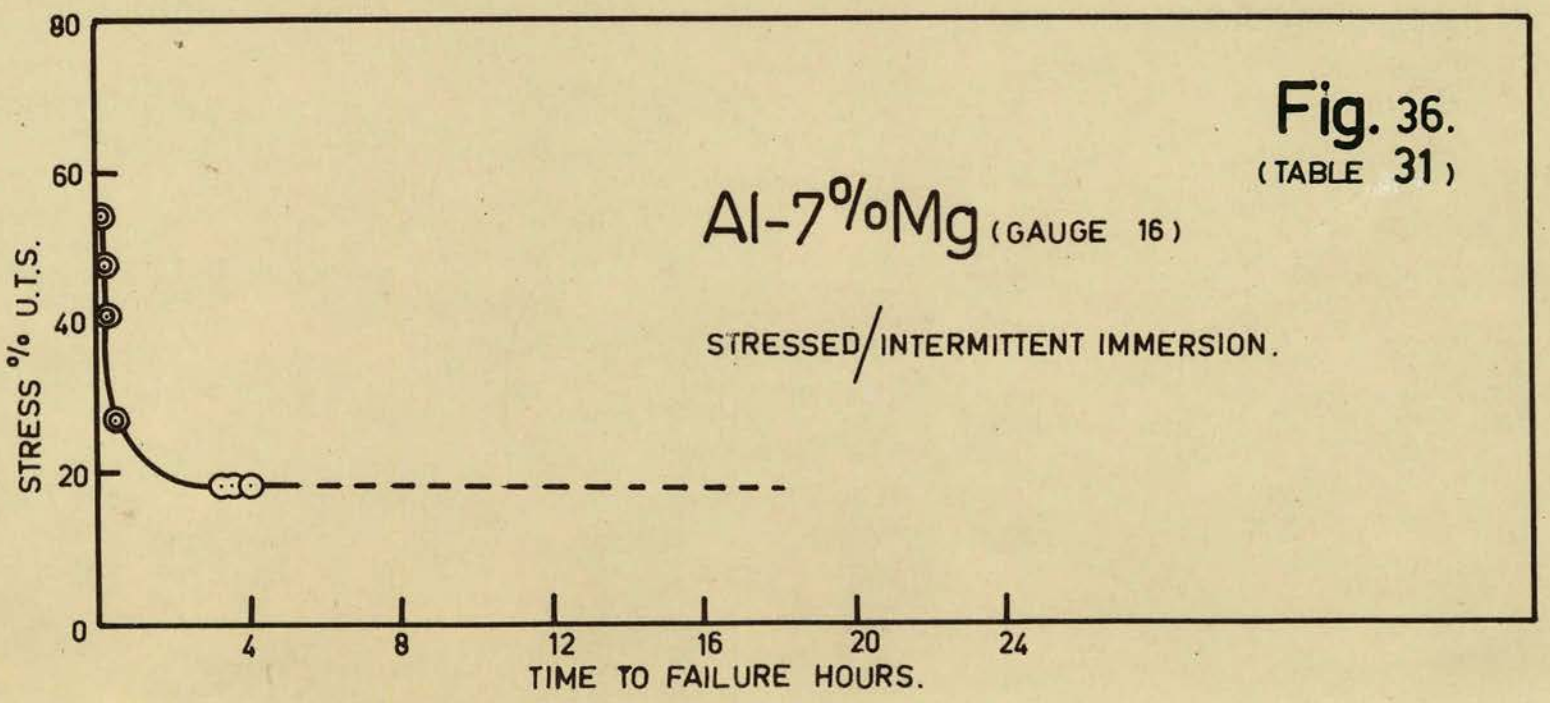


Fig. 36.

(TABLE 31)

Al-7%Mg (GAUGE 16)

STRESSED/INTERMITTENT IMMERSION.

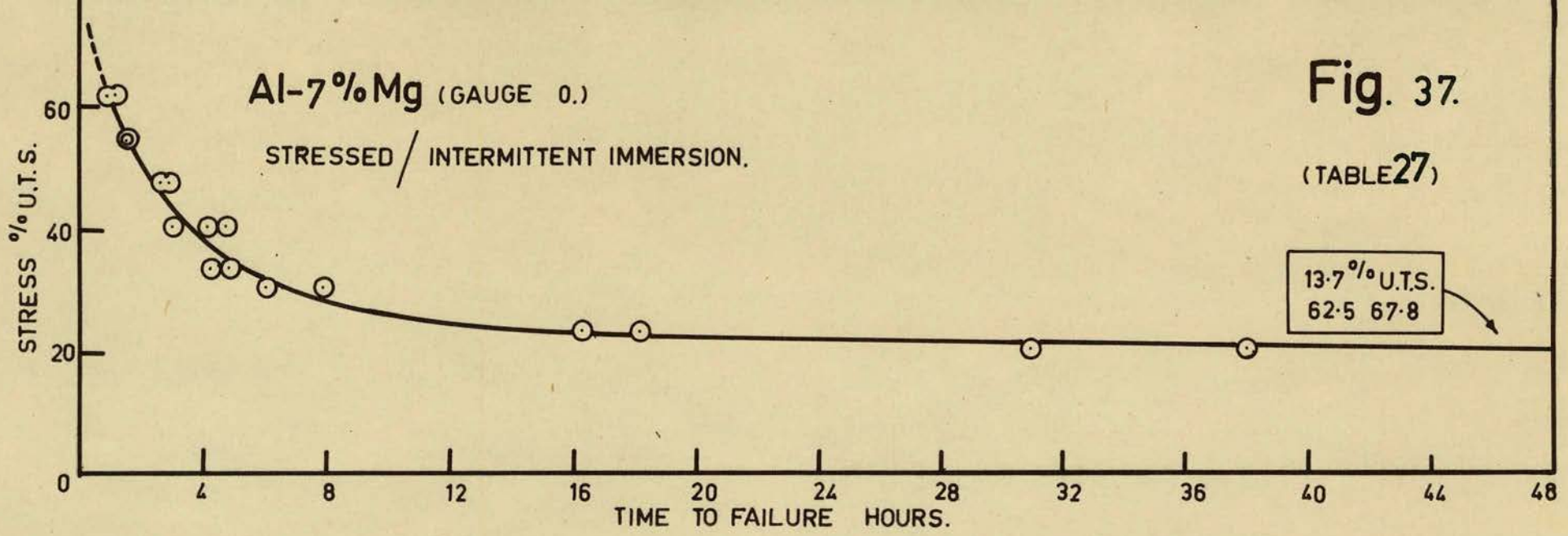


Fig. 37.

(TABLE 27)

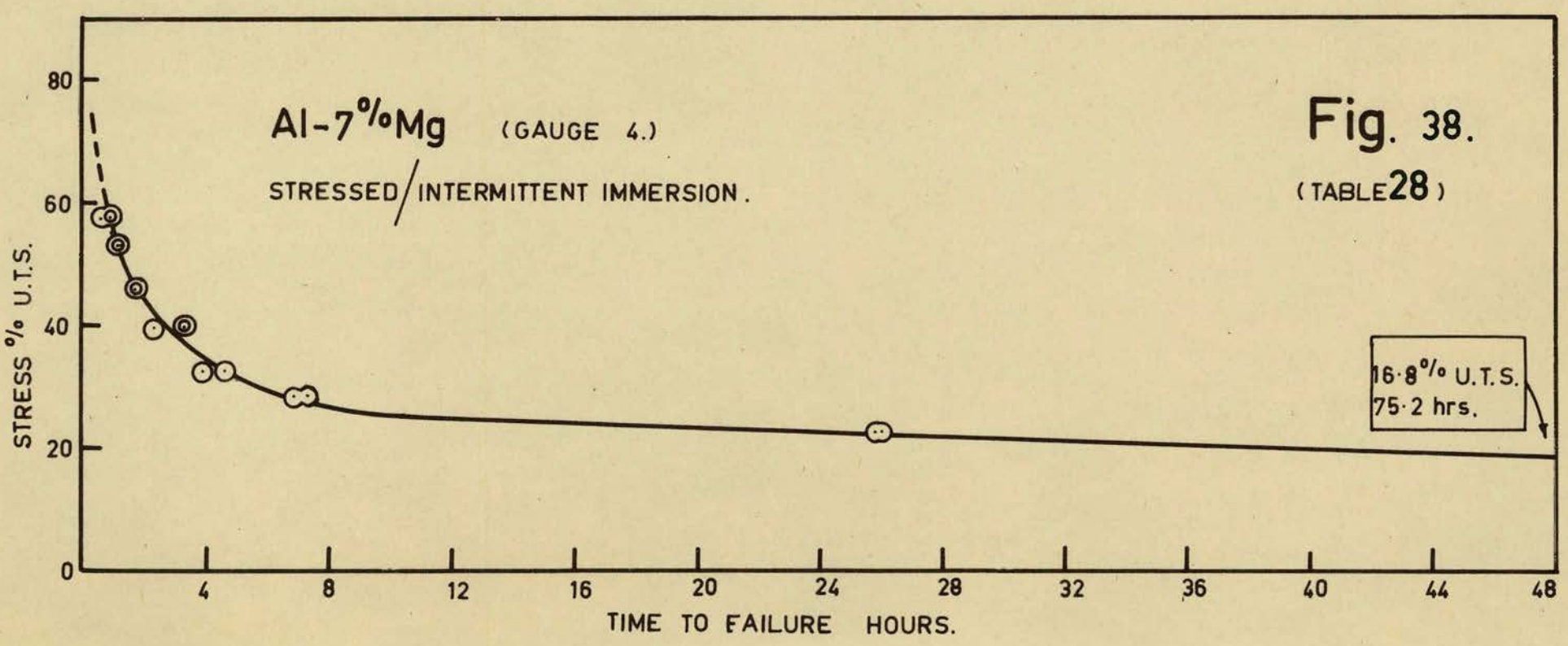


Fig. 38.

(TABLE 28)

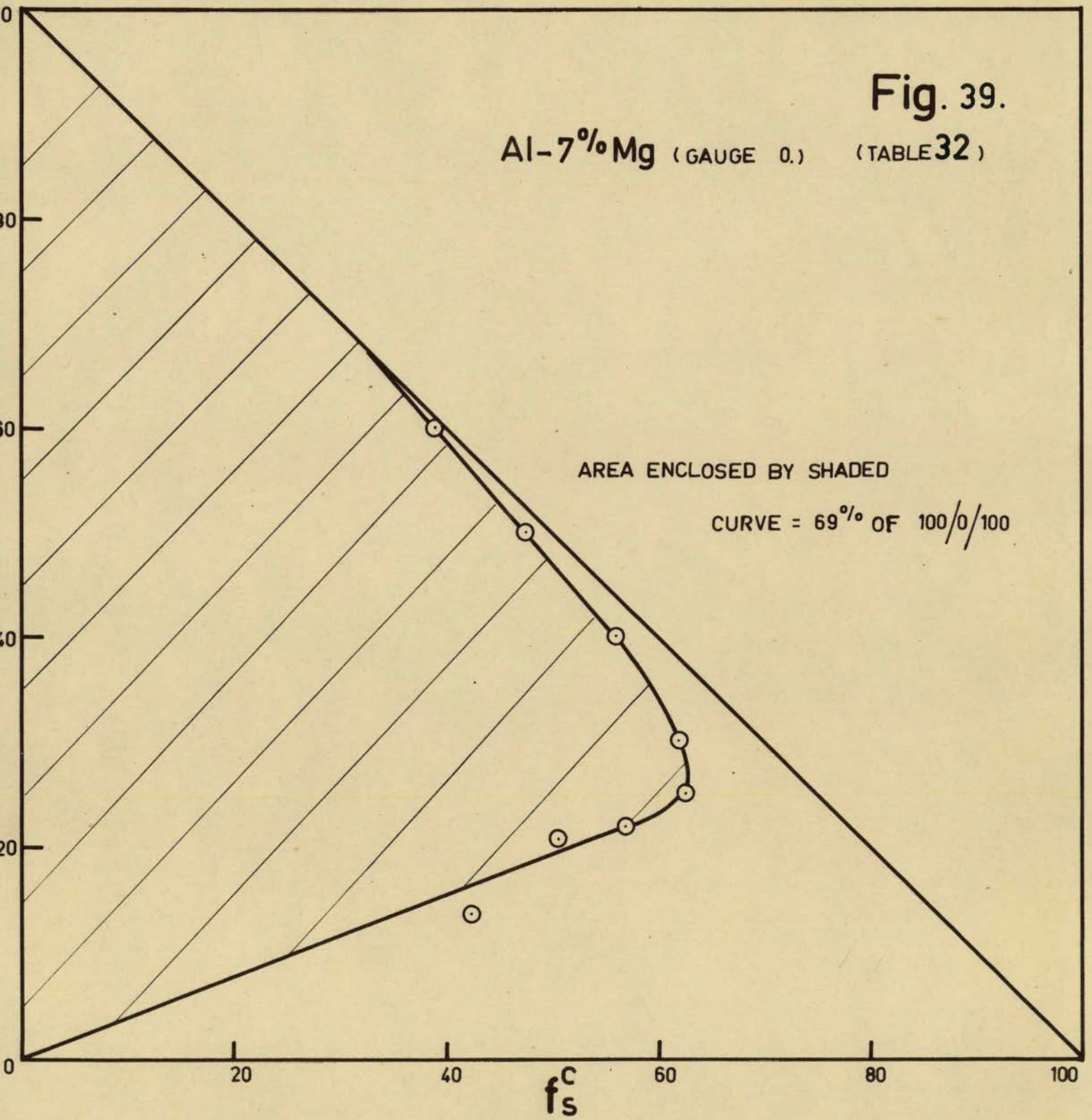


Fig. 39.
Al-7% Mg (GAUGE 0.) (TABLE 32)
AREA ENCLOSED BY SHADED
CURVE = 69% OF 100/0/100
0
20
40
60
80
100
f_s^c

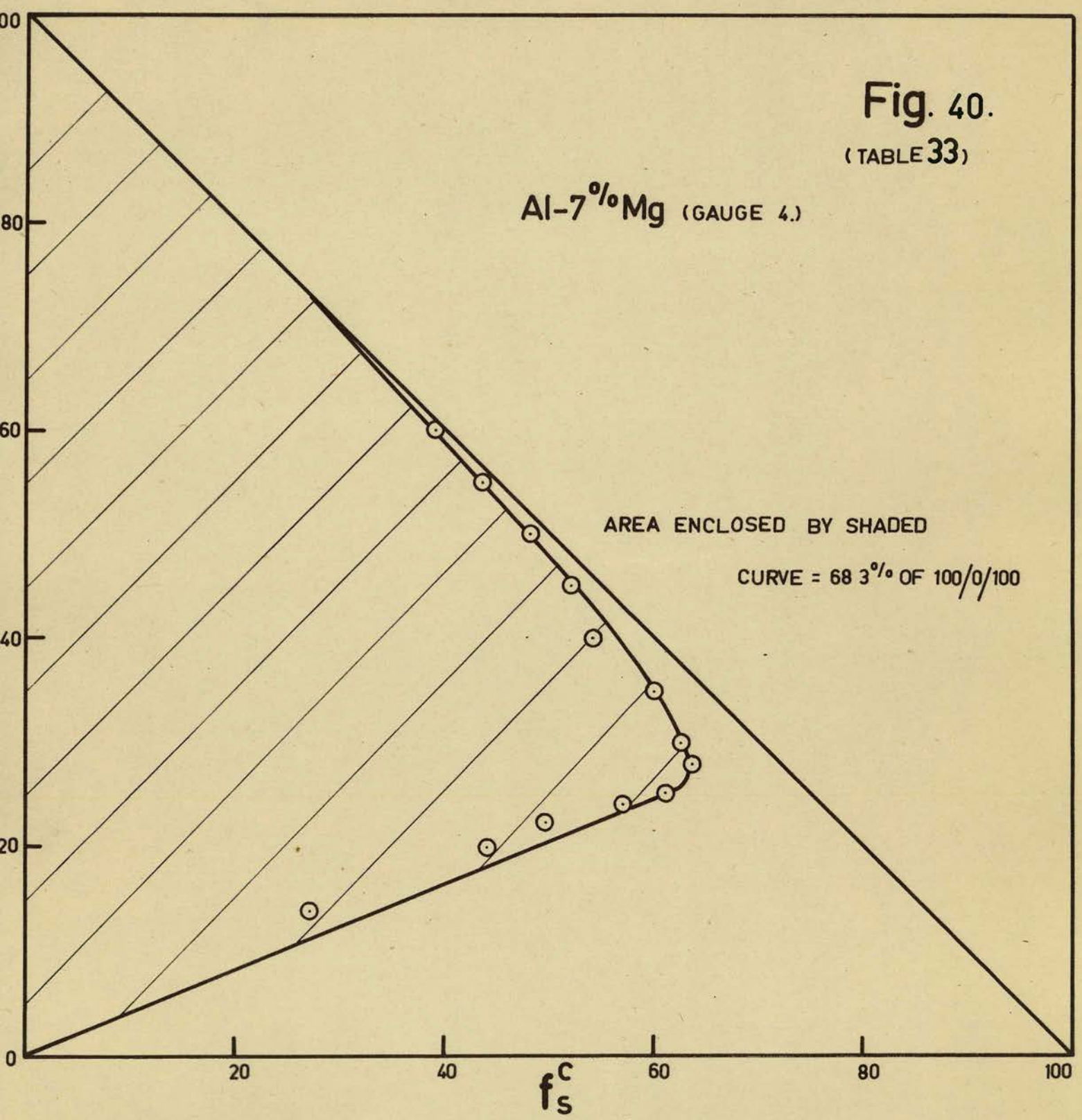


Fig. 40.
(TABLE 33)
Al-7% Mg (GAUGE 4.)
AREA ENCLOSED BY SHADED
CURVE = 68 3% OF 100/0/100
00
80
60
40
20
0
20
40
60
80
100
f_s^c

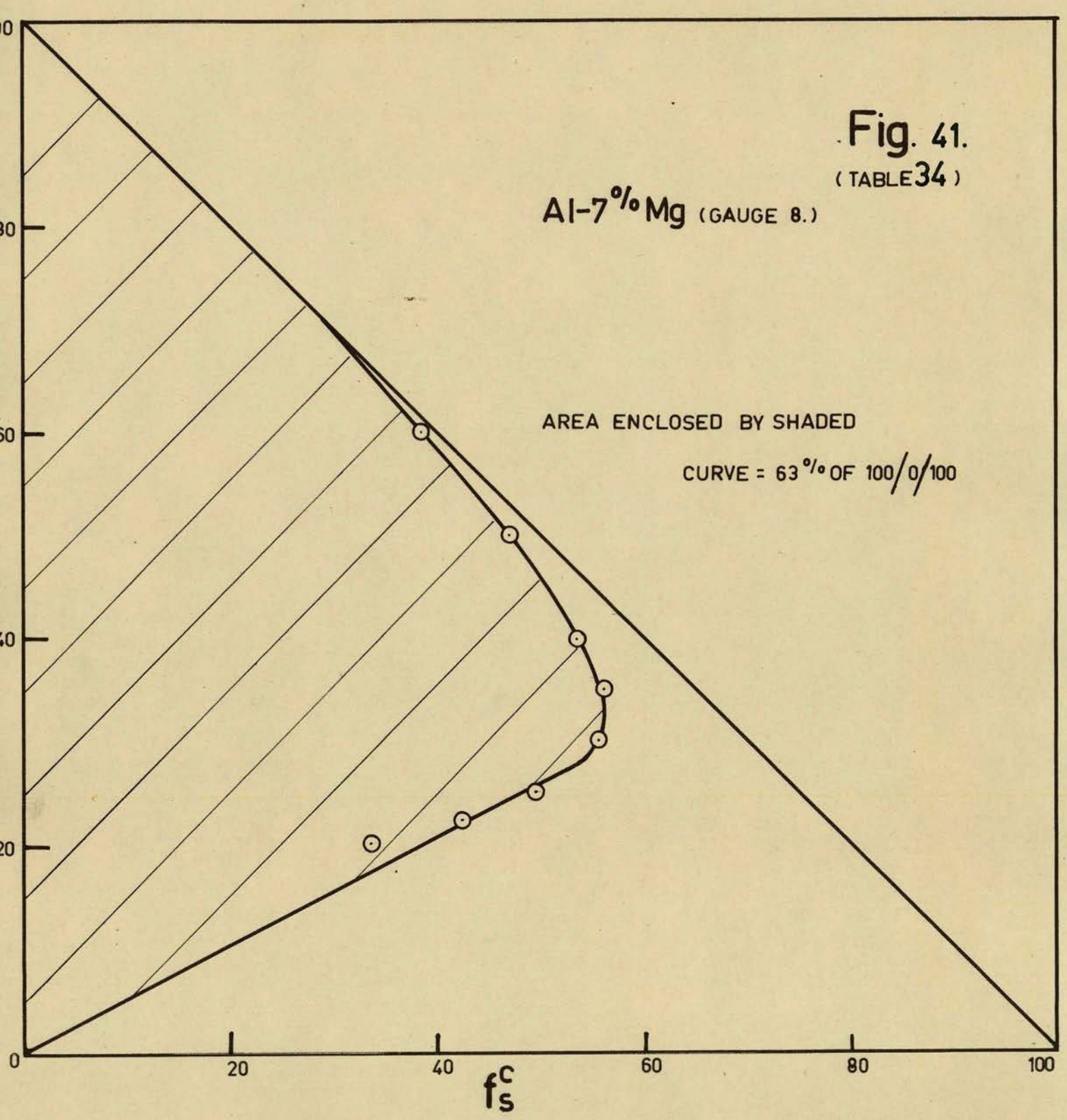


Fig. 41.
(TABLE 34)
Al-7% Mg (GAUGE 8.)
AREA ENCLOSED BY SHADED
CURVE = 63 % OF 100/0/100
0
20
40
60
80
100
f_s^c

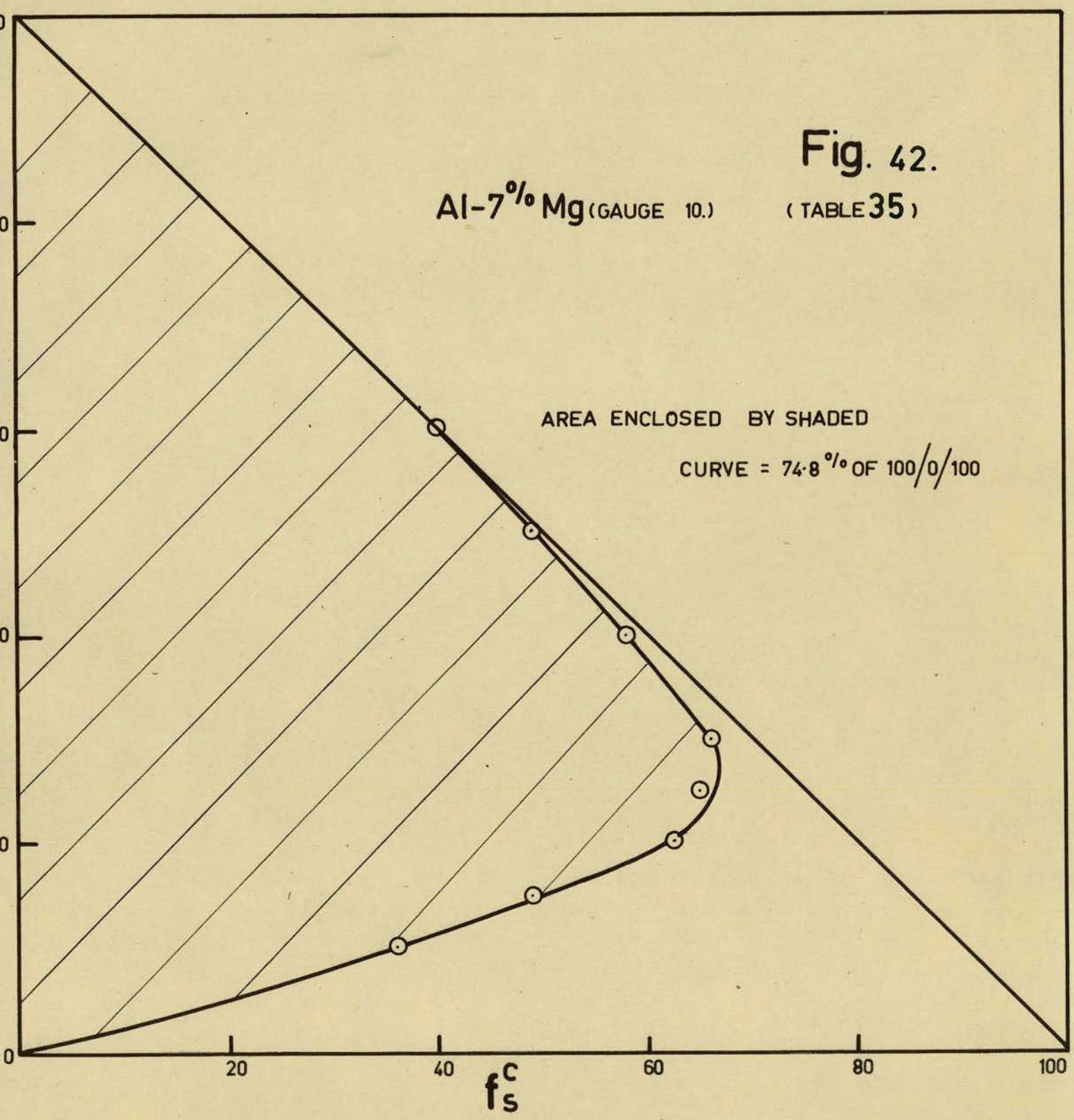


Fig. 42.
Al-7% Mg (GAUGE 10.)
(TABLE 35)
AREA ENCLOSED BY SHADED
CURVE = 74·8 % OF 100/0/100
0
0
0
0
0
20
40
60
80
100
f_s^c

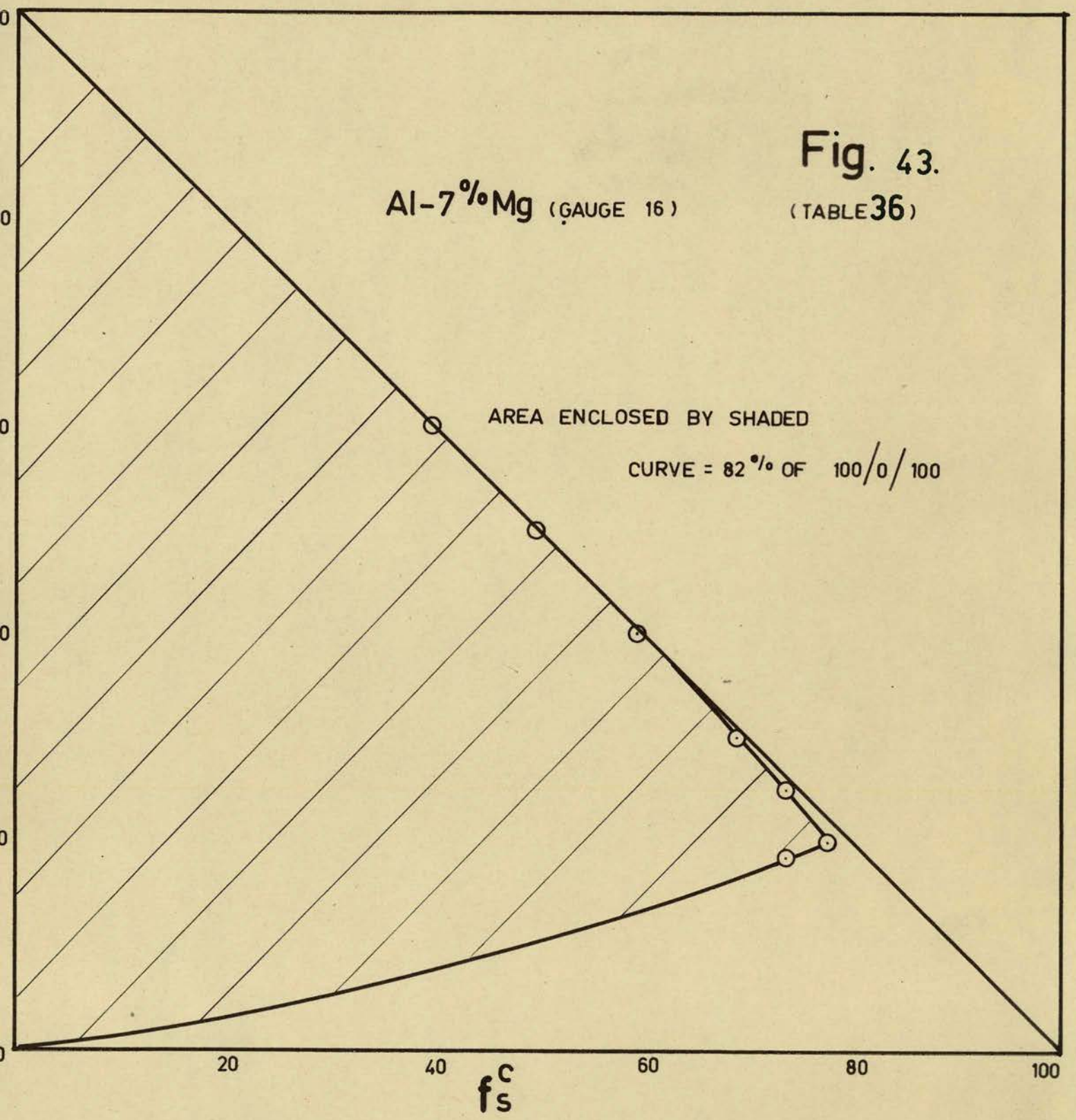


Fig. 43.
Al-7% Mg (GAUGE 16)
(TABLE 36)
AREA ENCLOSED BY SHADED
CURVE = 82 % OF 100/0/100
20
40
60
80
100
f_s^c

gauge O test-pieces after various periods of corrosion. After 24 hours exposure blisters of dimensions 2 x 2 mm. appeared on the otherwise unblemished metal surface and these after a further 24 hours became detached at one end and opened out flap-like. At the end of 72 hours a considerable amount of these metal flakes had collected in the bottom of each corrosion tube and vertical cracks appeared on the surface of the test-piece. By 200 hours the cracks had developed into deep fissures and over 80% of the U.T.S. had been lost. The formation of such blisters and flakes is probably due to a change in the direction of intergranular attack similar to that described in the case of the 3½%Mg alloy and shown in Figs. 9, 10 and 11. A continuous evolution of hydrogen was observed during the unstressed corrosion of all gauges of the 7%Mg alloy and appeared to increase with the breaking up of the metal surface. Failures of the heavier gauges of test-pieces were observed to take place in three clearly defined stages. From its first appearance the crack slowly widened over a considerable number of immersion cycles. The development was uniform until the crack was about 15/1000 inch wide and extended around the specimen for about 1/3 of the

circumference. On the following immersion cycle, as soon as the liquid level passed the crack, rapid extension took place resulting in a sudden jerk of the spring. No further movement took place during this cycle nor in the succeeding "dry" cycle but failure almost invariably occurred on the next immersion cycle as soon as the corrosive solution reached the crack.

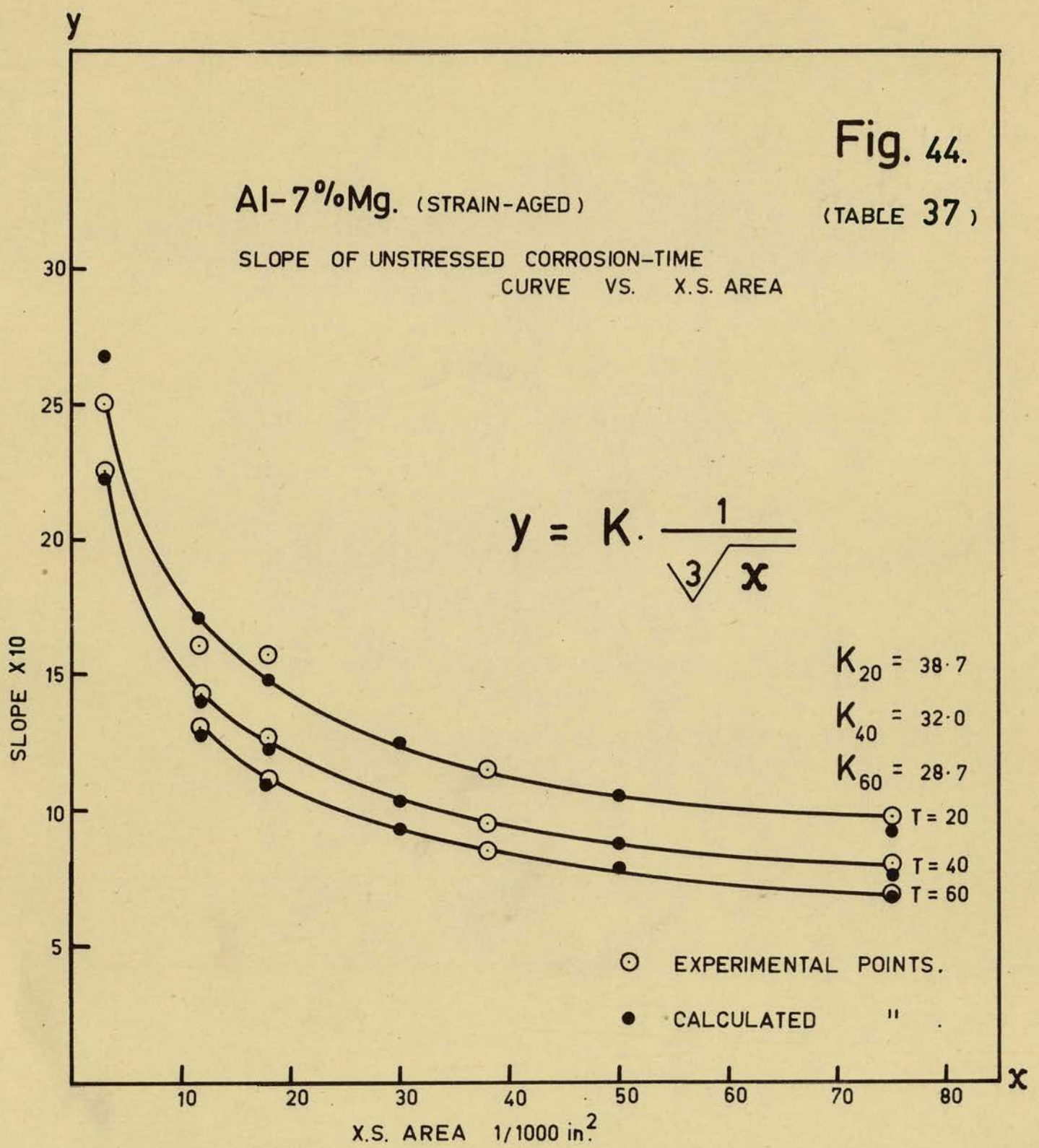
Stress-corrosion susceptibility curves were extrapolated to pass through the origin as in the case of the gauge 16 7% Mg alloy used in Experimental Part II. (q.v.) It can be seen from the unstressed corrosion-time curves that with the exception of gauge 8 all other gauges showed unstressed losses up to 90% of the U.T.S. and extrapolation to the origin was considered preferable to the carrying out of prolonged tests at very low applied stresses. The reproducibility of times-to-failure at such low loads would be of a low order and errors in the derived f_s^c values would probably exceed the small error introduced into the value of the stress-corrosion susceptibility by extrapolating to the origin when the intercept on the stress axis should be say 3%.

The unstressed corrosion-time for all gauges

of the alloy show a comparatively uniform rate of loss of strength with time up to 80% loss of U.T.S. The slopes of the curves were examined, therefore, to determine if they were in any way related to the cross-section of the specimens used in their construction. The portion of the unstressed curve which is necessary for the calculation of S_s^c is directly related to the observed time-to-failure corresponding to the minimum applied stress required to define clearly the applied-stress vs. time-to-failure curve for each gauge. The unstressed curves were examined, therefore, within the region 0-60 hours on the common time axis. It was found that the approximate slope of the unstressed corrosion-time curve for each gauge of test-piece was proportionsl to the reciprocal of the cube root of the cross-section of the test-piece. The relationship may be expressed as:-

$$Y = K. \frac{1}{\sqrt[3]{X}}$$

where Y is the slope and X the cross-section. The plot of the equation is shown in Fig. 44, Table 37. The values of K within the time axis limits of 0-20, 0-40 and 0-60 are calculated although the accuracy


y
Fig. 44.
(TABLE 37)
Al-7%Mg. (STRAIN-AGED)
SLOPE OF UNSTRESSED CORROSION-TIME CURVE VS. X.S. AREA
$y = K \cdot \frac{1}{\sqrt[3]{x}}$
K_{20} = 38·7
K_{40} = 32·0
K_{60} = 28·7
T = 20
T = 40
T = 60
EXPERIMENTAL POINTS.
CALCULATED "
SLOPE X10
30
25
20
15
10
5
10
20
30
40
50
60
70
80
x
X.S. AREA 1/1000 in.^{2}

shown is not claimed. It is suggested, however, that the corresponding slopes for intermediate cross-sections can be derived from the relationship expressed above within the accuracy of experimentally derived values. The validity of the relationship is only claimed for Al-7%Mg., for the cross-sections used and for the experimental conditions, although it is possible that it may be extended to include similar alloys of different magnesium content and cross-sections greater than those described in this thesis.

DISCUSSION. Part III.

DISCUSSION Part III See Experimental Part III.

For specimens of a given aluminium alloy of similar cross-section but different cross-sectional area the amounts of metal lost by corrosion per unit of exposed surface should be equal, assuming general corrosion, for equal periods of exposure. The rate of loss of % U.T.S. of these specimens would however be expected to differ in a manner related to the area of the specimen cross-sections. Unstressed corrosion-time curves of Al-7%Mg specimens of varying cross-section are shown in Figs. 29, 30, 31, 33, and 35 and Tables 22, 23, 24, 25 and 26. It can be seen that the initial slopes of these curves become progressively greater as the cross-sectional areas of the specimens decrease. For example after 40 hours exposure % loss of U.T.S. for 0, 4, 8, 10 and 16 was 30, 40, 50, 60 and 90 respectively. The curves can be divided into three groups as follows:- Group I consisting of gauges 0 and 4, Group II, gauges 8 and 10 and Group III, gauge 16. It is proposed to treat these groups separately.

Group I.

The curves of gauge 0 and 4 specimens are

similar in that they deviate from the exponential law which usually governs the corrosion of Al/Mg alloys. (106) It was observed that extensive longitudinal splitting of the corroded surface layers took place after about 100 hours exposure. (Fig. 49) With respect to oxide films on aluminium it has been shown that if M is the molecular weight of the oxide, D its density, m the weight of metal contained in M of oxide and d the density of the metal then $Md/mD > 1$ (107) i.e. the bulk of the oxide product is greater than the metal converted and the oxide film is in a state of compression. It is suggested that this is true to an even greater degree for the unremoved corrosion products of Al/Mg alloys and that the compression in the film will be higher since the hydrated form of the oxide will be the more bulky. In the case of a specimen of circular cross-section there is a probability that these compressive stresses will be unbalanced due to the presence of a radial component acting outward from the zone of active corrosion where new and active corrosion product is being produced. It is suggested that the longitudinal splitting described above is the result of this outward thrust.

Group II.

Gauge 8 and 10 unstressed curves tend to become asymptotic after approximately 100 hours exposure showing that film thickness has reached the critical stifling value. Assuming that the penetration of corrosion is uniform over the entire exposed surface of the alloy then the metal destroyed in each specimen will occupy a concentric annulus on the outside of the cross-section. From the losses of U.T.S. observed for each gauge of specimen at exposure times of 25, 50, 100 and 150 hours the thickness or radial depth of these annuli have been calculated. (Table 38) The depth corresponding to 100 hours exposure, i.e. the time at which the asymptote appears, was 0.05 inches and can be used as a yard-stick to denote the film thickness at which stifling occurs. The term film thickness is used loosely since in the case of intergranular corrosion the critical film is also intergranular and the annulus described above can be regarded as a zone of detached or semidetached crystals each surrounded by corrosion product. It can be seen that the path of diffusion through such a system is unlikely to be directly along a radius. The existence of the asymptotes indicates that failure of the film did not

take place and certainly no longitudinal splitting, as occurred with the 0 and 4 gauges, was observed. The reason for the absence of splitting is probably associated with the internal diameter of the annulus in the same way that for the same wall thickness a narrow bore tube can withstand without failure a higher pressure than a tube of wider bore, i.e. the total compressive force acting outward increases with internal diameter while the annulus depth which determines the strength of the annulus remains the same.

Group III.

It has been shown that the asymptote of the 8 and 10 gauge specimens occurs after about 100 hours and that the depth of the annulus of corroded metal at this time is 0.05 inches. On any diameter of any specimen the total linear corrosion will be therefore 2 x 0.05 or 0.1 inch. The diameter of the 16 gauge specimen is 0.06 inches and it can be seen that total loss of U.T.S. will occur before film thickness, corresponding to an annulus depth of 0.05 inches, is reached and so an asymptote will not occur. This is the converse of the case of the 0 and 4 gauge specimens in which it is believed

that the film increased in thickness to the asymptote value of 0.05 inches (annulus) at about 100 hours and then split up because its strength was not sufficient to withstand the outward radial component of its self-compression.

The depth of penetration of corrosion for each gauge of specimen at different values of exposure time (T) are shown in Table 38. Values were not calculated where asymptotes occurred at or near the values of T chosen, e.g. gauge 8 and 10 at 100 and 150 hours. In the case of 16 gauge specimens total loss of U.T.S. took place at about 48 hours and depth of penetration is only shown for T = 25 hours. The results show that the depth of penetration in the initial stages, i.e. up to 60-70% loss of U.T.S., is independent of the cross-section for the alloys described in Experimental Part III.

The average slopes of the unstressed curves of the various gauges were determined for the exposure time intervals 0-20, 0-40 and 0-60 hours. These were plotted against cross-section area as shown in Fig. 44. If Y is the slope and X the cross-section then the equation for the three curves is

$$Y = K.\frac{1}{\sqrt[3]{X}}$$

The values of K for the exposure time intervals shown are 39, 32 and 29. The rate of loss of U.T.S. of Al-7%Mg rods, strain-aged 10% and 125°C/24 hours and corroded unstressed by intermittent immersion is therefore inversely proportional to the cube root of their cross-section area. It should be noted that this relationship is only claimed for sections of the curves between the origin and 60 hours exposure time. These were the only regions of the unstressed curves which were involved in the determination of the stress-corrosion susceptibilities since failures at greater than 60 hours were not observed.

The stress vs. time-to-failure curves for the various gauges are shown in Figs. 37, 38, 32, 34 and 36, and Tables 27, 28, 29, 30 and 31. With the exception of gauge 8 times-to-failure for all applied stresses decreased with decrease in specimen cross-section. The inflections of the curves at the region of the threshold stresses were more sharp for the smaller cross-sections. At applied stresses of 25% and 30% U.T.S. gauge 8 specimens showed higher times-to-failure than specimens of gauge 0 and 4 when the overall picture at higher stresses suggested that these times would

be shorter. For example at an applied stress of 50% U.T.S. times-to-failure for gauges 0, 4, 8, 10 and 16 were 2.0, 1.3, 1.0, 0.5 and 0.17 hours and at 40% U.T.S. were 3.6, 2.7, 2.4, 1.1 and 0.27 hours. The wide spread of results in the unstressed corrosion-time curve of the gauge 8 alloy and the development of bends in the corroded specimens resulting in large changes in their corrosion patterns have been mentioned previously.

Times-to-failure of different gauges were plotted against cross-section for various applied stresses as shown in Fig. 52. Gauge 8 results have been omitted because of uncertainty felt as to their reliability. It can be seen that there is a general tendency for the curves to become asymptotic to a line representing a limiting time-to-failure. The asymptote is more clearly defined at the lower stress values and appears to occur above a cross-section of 0.1 square inches, or S.W.G. 000. Further speculation along these lines is not possible in the absence of more complete data on the corrosion behaviour of alloy specimens of cross-section greater than this value. The relationship between cross-section, applied stress

and time-to-failure for specimens of gauge 0, 4, 10 and 16 are shown in Fig. 45.

As observed previously the majority of failures which took place under direct observation appeared to occur at the beginning of an immersion cycle. Cracks first became visible some 2-5 minutes, depending on the gauge size, before failure and slowly became more sharply outlined. This was a gradual process and it is not certain whether or not it continued during the "dry" cycle. The gradual widening was followed by an instant of sudden yielding during which the crack increased in width by about four times. This coincided with the appearance of subsidiary cracks closely adjacent to and parallel to the main crack. A period of stasis during the next "dry" cycle preceded sudden failure which occurred at the moment of first contact with the corroding solution. It is generally agreed that during the unstressed corrosion of Al/Mg alloys a great many boundaries are attacked but when stress is applied corrosion is restricted to one or perhaps two paths. Fig. 51 shows a number of specimens in which two cracks were proceeding almost simultaneously. The cracks shown are those resulting from the first rapid yielding which occurred within approximately 5 minutes of their

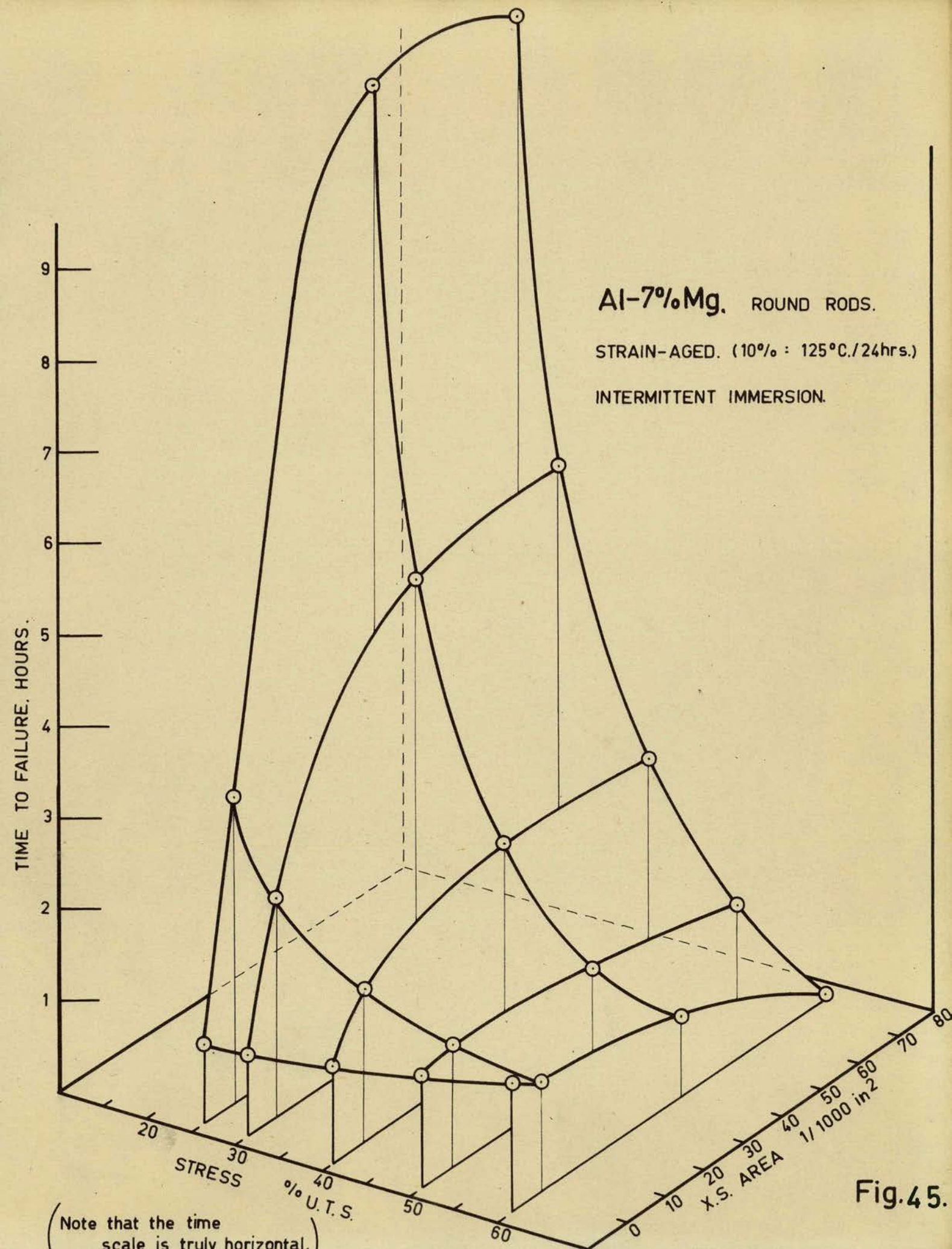

Al-7%Mg. ROUND RODS.
STRAIN-AGED. (10% : 125°C./24hrs.)
INTERMITTENT IMMERSION.
TIME TO FAILURE, HOURS.
1
2
3
4
5
6
7
8
9
STRESS % U.T.S.
20
30
40
50
60
X.S. AREA 1/1000 in²
0
10
20
30
40
50
60
70
80
(Note that the time scale is truly horizontal.)

Fig.45.

first appearance, i.e. immediately after the period of gradual "yawning" (Evans) and would normally have resulted in failure if the specimen had not first failed elsewhere. The photographs are of interest in that they show stress-corrosion cracks during their most active stage of propagation. It is quite certain that these cracks would have proceeded to failure at the beginning of the next immersion cycle, i.e. within the next two minutes.

The stress-corrosion susceptibilities for the various gauges of specimens are shown in Figs. 39, 40, 41, 42 and 43, Tables 32, 33, 34, 35 and 36. These were 69.0, 68.3, 63.0, 74.6 and 82.0 for gauges 0, 4, 8, 10 and 16 respectively. It can be seen that susceptibilities tend to increase in value as the cross-section of the specimens decreases. The rather low value of gauge 8 is thought to be due to the poor reproducibility of loss of % U.T.S. obtained during unstressed corrosion. This is clearly shown in Fig. 31 and as previously stated was due to bending of specimens during corrosion.

If the rate of propagation of a stress-corrosion crack, excluding the very short period of

actual failure, is independent of specimen cross-section then times-to-failure for the same applied stress should increase with increase of cross-section. This has been observed. S_u^c is a direct function of time-to-failure and will increase therefore with increase of gauge size. On the other hand the slope of the unstressed curves increases with reduction in cross-section and since S_u^c is also directly related to this slope there will be a tendency for it to decrease with increase in gauge size. From Fig. 52 it can be seen that when the applied stress is reduced from 50% to 25% U.T.S. times-to-failure are increased by a factor of 6-8 in the case of gauges 0, 4 and 10 but for gauge 16 the factor of increase is about 3, i.e. about half as much. The increased times-to-failure for gauges 0 and 4 were 11.6 and 11.0 hours respectively and for gauges10 and 16, 3.2 and 0.53 hours. It is clear that in the case of gauge 16 the smaller proportional increase in time-to-failure at low applied stresses is not adequately compensated by the increased slope of its unstressed curve associated with its small cross-section. Values of S_u^c will therefore be disproportionately smaller for cross-sections

corresponding to and less than gauge 16. S_s^c, which by definition requires failure of the specimen regardless of the time-to-failure, depends only on the magnitude of the applied stress, i.e. S_s^c = 100% U.T.S. - Load (as % U.T.S.) causing failure. For the same applied stress S_s^c will be constant for all gauges of specimen. Since $f_s^c = S_s^c - S_u^c$ and the area of the curve f_s^c vs. applied stress is directly proportional to f_s^c a lower stress-corrosion susceptibility is obtained for gauge 16 specimens. The effect will probably be more marked in the case of specimens of still smaller cross-section. Comparison of stress-corrosion susceptibilities derived by the method of Jones (3) can only be made .·. on a basis of equal cross-section of all contributing experimental specimens.

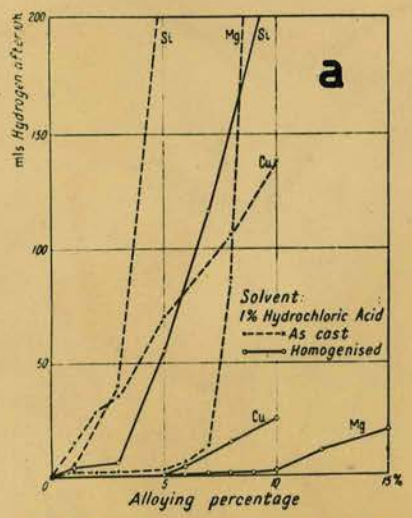


Fig. 508. Behaviour of binary aluminium alloys in the "as cast" and homogenised states in a 1% solution of hydrochloric acid. (According to Vosskühler, *Z. Aluminium*, 1938.)

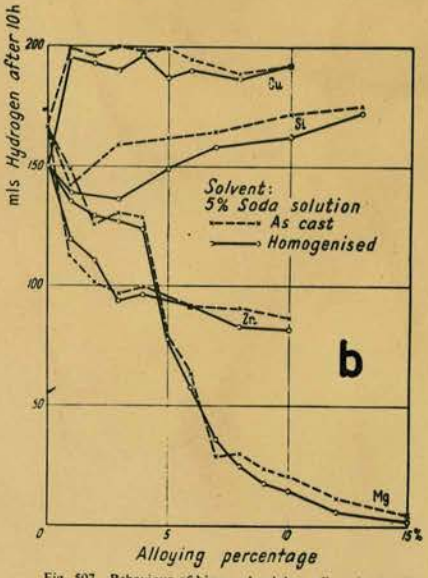
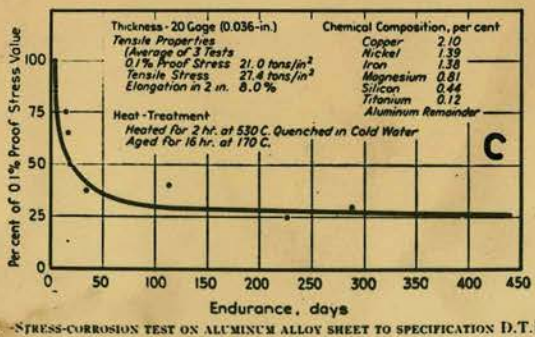
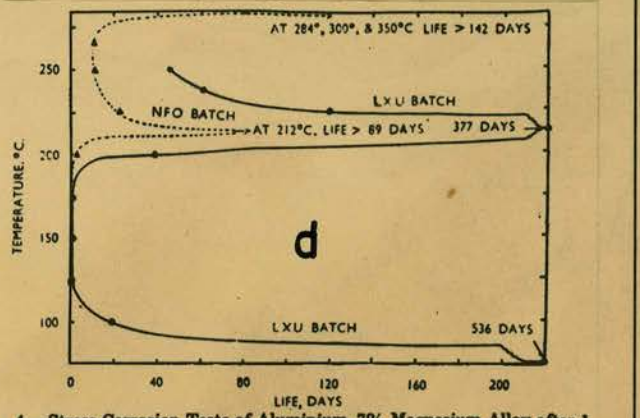


Fig. 507. Behaviour of binary aluminium alloys in the "as cast" and homogenised states in a 5% soda solution. (According to Vosskühler, *Z. Aluminium*, 1938.)



c. STRESS-CORROSION TEST ON ALUMINUM ALLOY SHEET TO SPECIFICATION D.T.D. 206.

Note: 21.0 Tons = 47,000 lb. 530 C. = 1100 F.
27.4 Tons = 61,400 lb. 170 C. = 340 F.



4.—Stress-Corrosion Tests of Aluminium–7% Magnesium Alloy after 1 week's artificial ageing. Initial tensile stress 9·5 tons/in.²

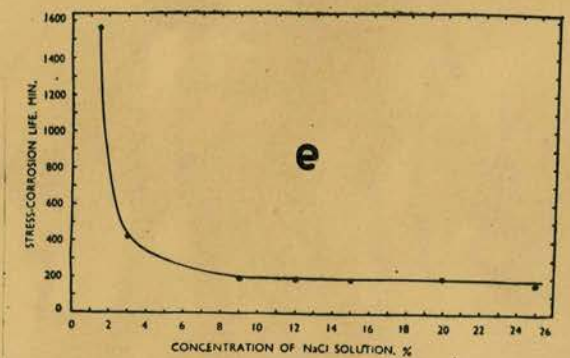
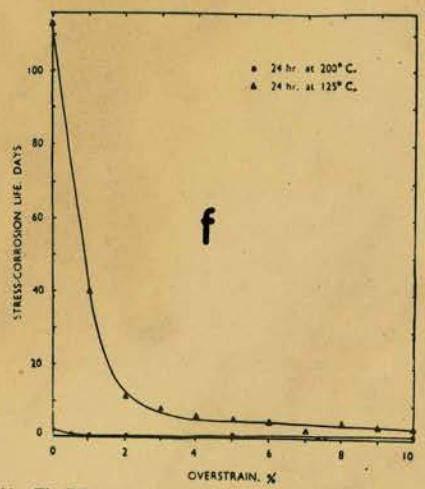


FIG. 6.—Effect of Concentration of Sodium Chloride Solution on Stress-Corrosion Life of Aluminium–7% Magnesium Alloy.



10.—The Effect of Pre-Overstrain on the Stress-Corrosion Life of an Aluminium–7% Magnesium Alloy.

Fig. 46.

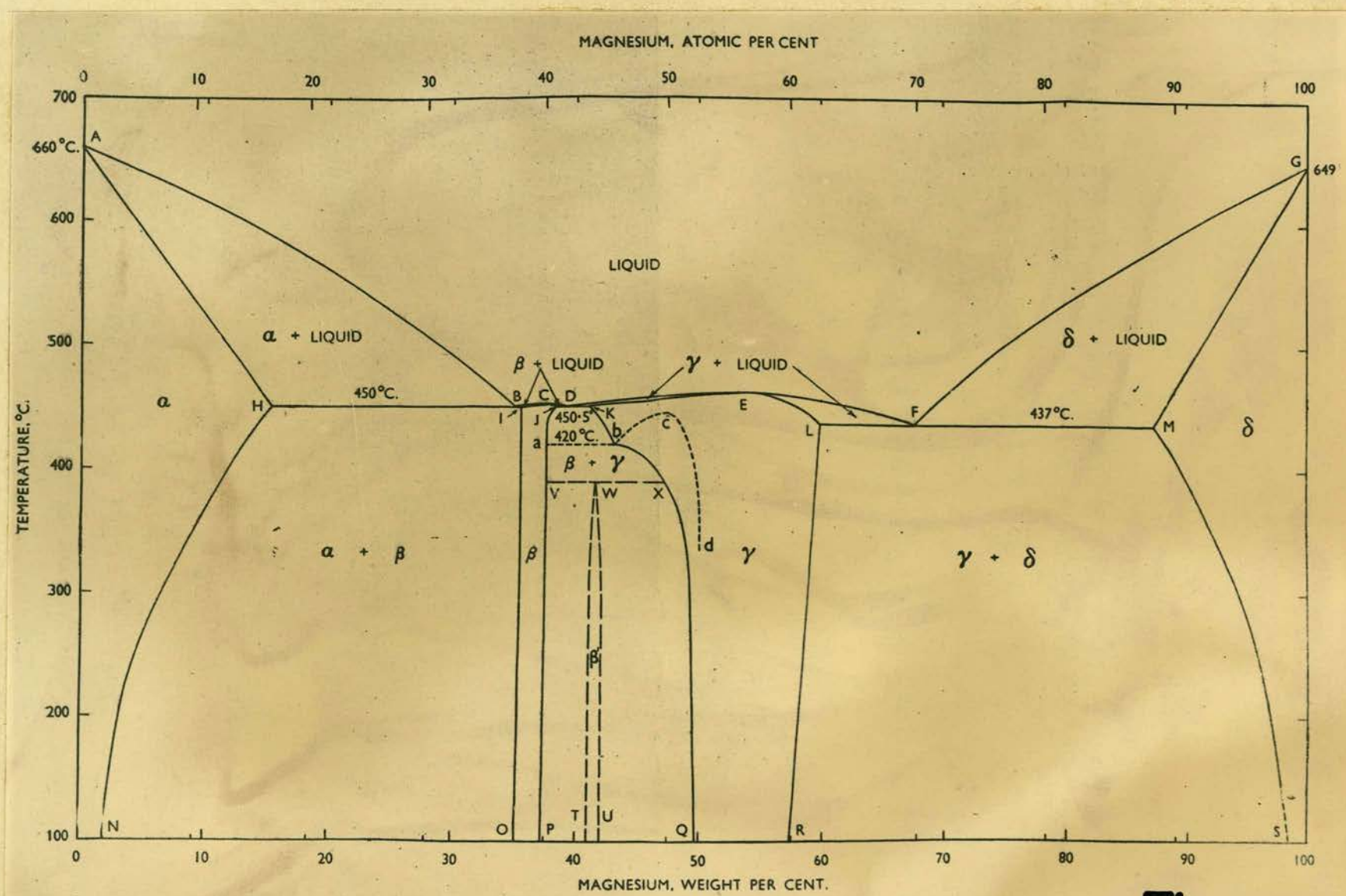

MAGNESIUM, ATOMIC PER CENT
0
10
20
30
40
50
60
70
80
90
100
700
660 °C.
600
500
400
300
200
100
TEMPERATURE, °C.
A
G
649
LIQUID
α + LIQUID
β + LIQUID
γ + LIQUID
δ + LIQUID
α
450°C.
H
B
C
D
I
J
450·5
K
E
F
437°C.
M
δ
L
420°C.
a
b
c
d
β + γ
V
W
X
α + β
β
γ
γ + δ
β
N
O
P
T
U
Q
R
S
MAGNESIUM, WEIGHT PER CENT.

Fig. 47.

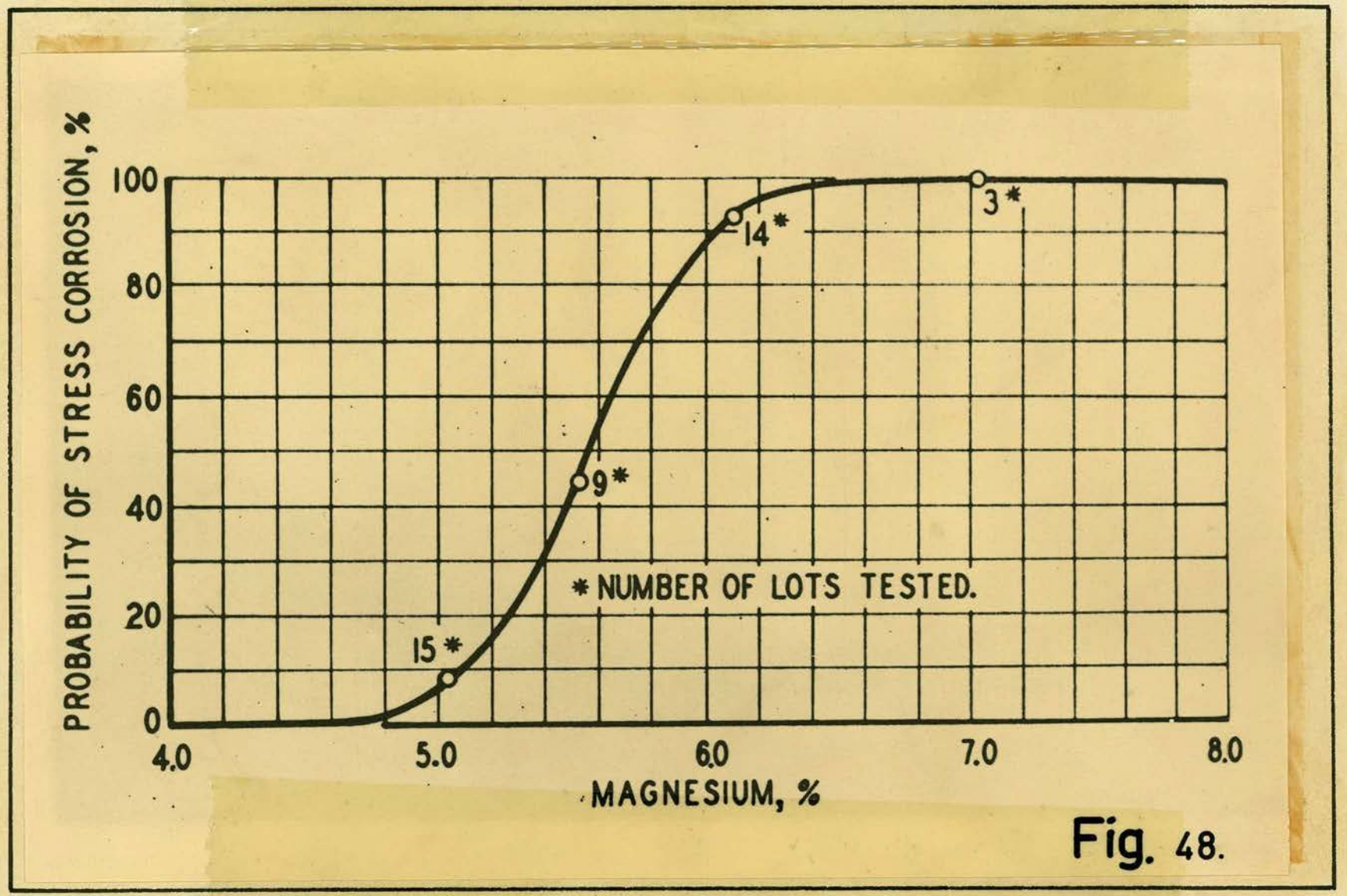
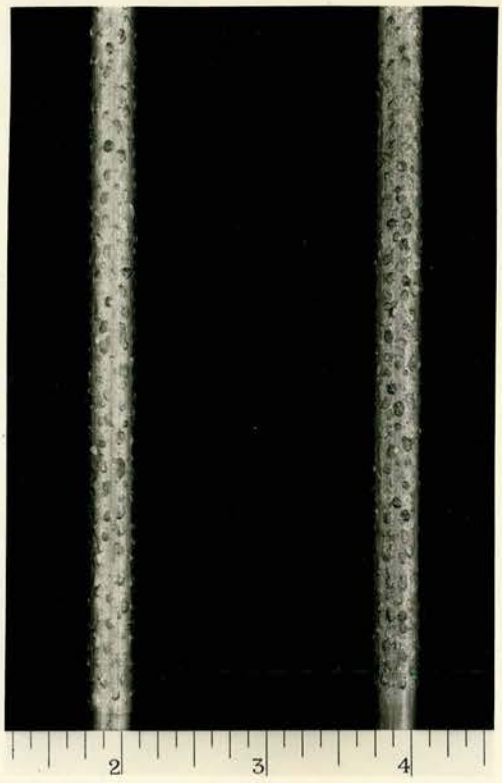
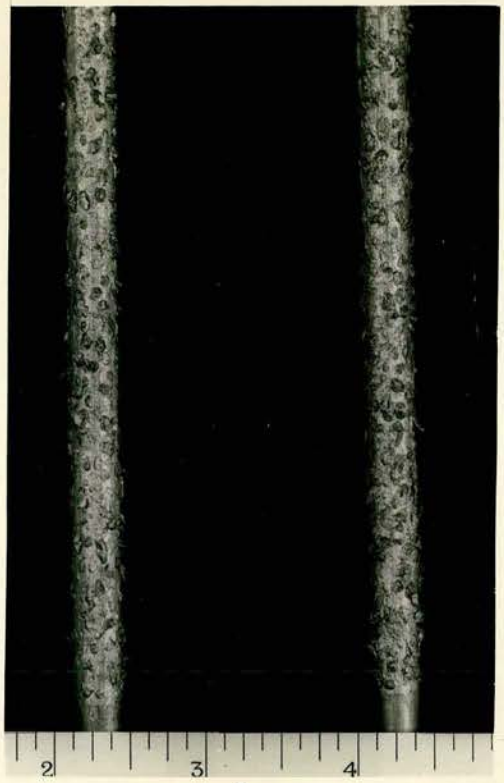


Fig. 48.

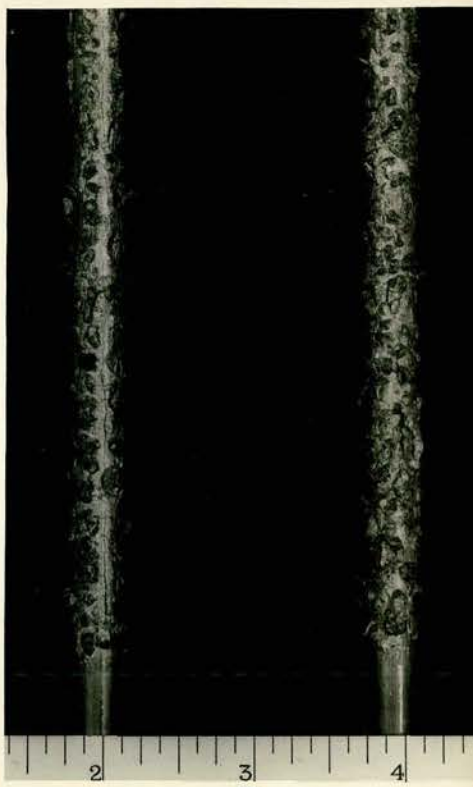
E.H. DIX. TRANS. AMER. INST. MIN. MET. ENG. 1940, 137, 11.



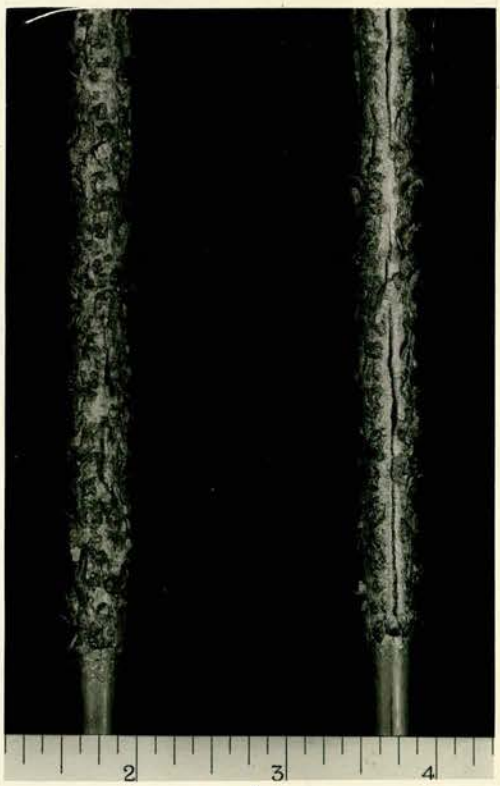
a.



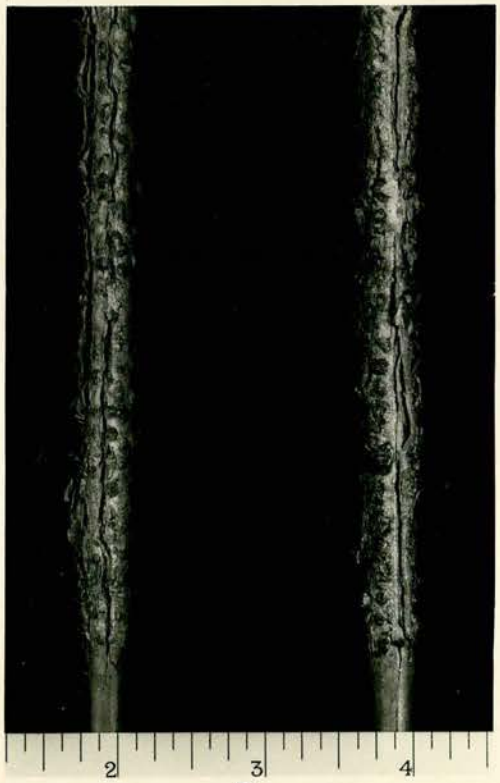
b.



c.



d.



e.

Al-7% Mg. GAUGE 0.

UNSTRESSED.

INTERMITTENT IMMERSION.

a. 24 hours.

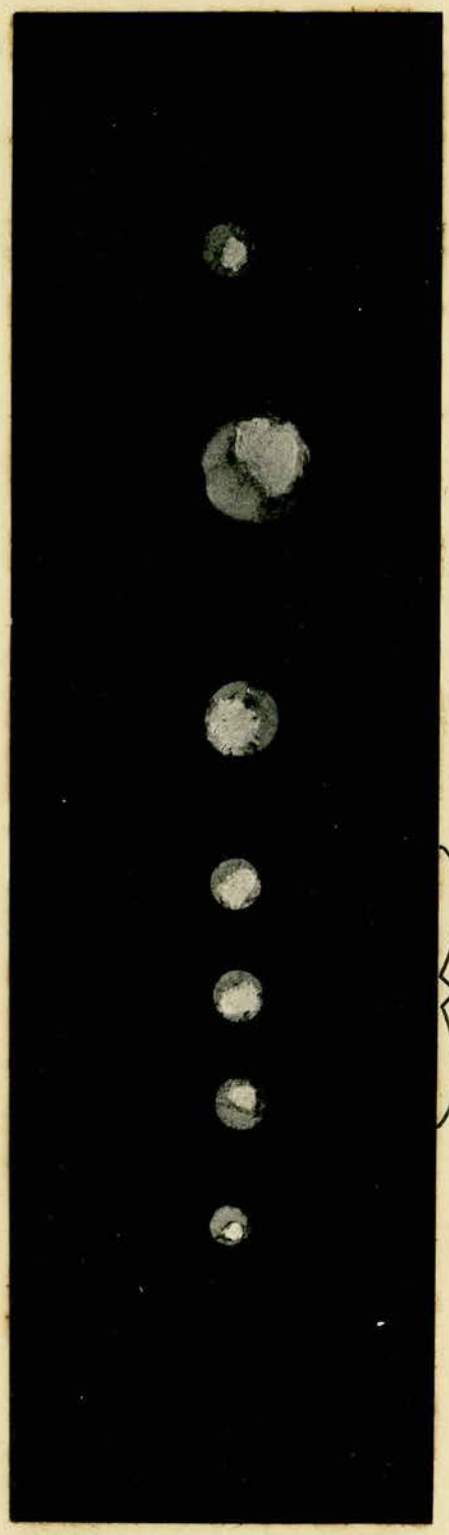
b. 48 "

c. 72 "

d. 120 "

e. 195 "

Fig. 49.



Al-7%Mg.

B.S.W.G. 8.

" 0.

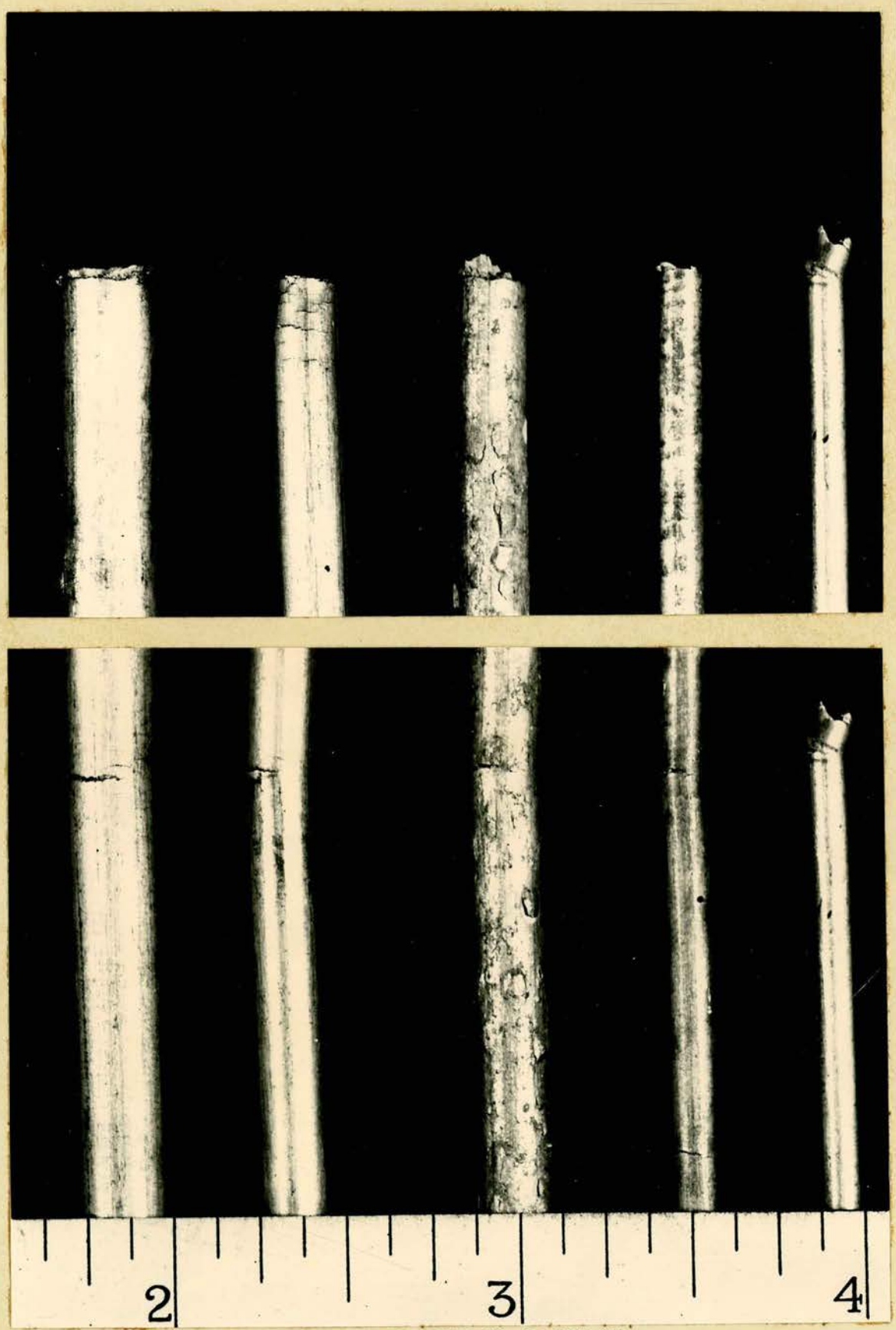
" 4.

" 8.

" 10.

Fig. 50.

STRESS-CORROSION CRACKS. X1·5 APPROX.



SECONDARY STRESS-CORROSION CRACKS IN Al-7% Mg.

Fig. 51.

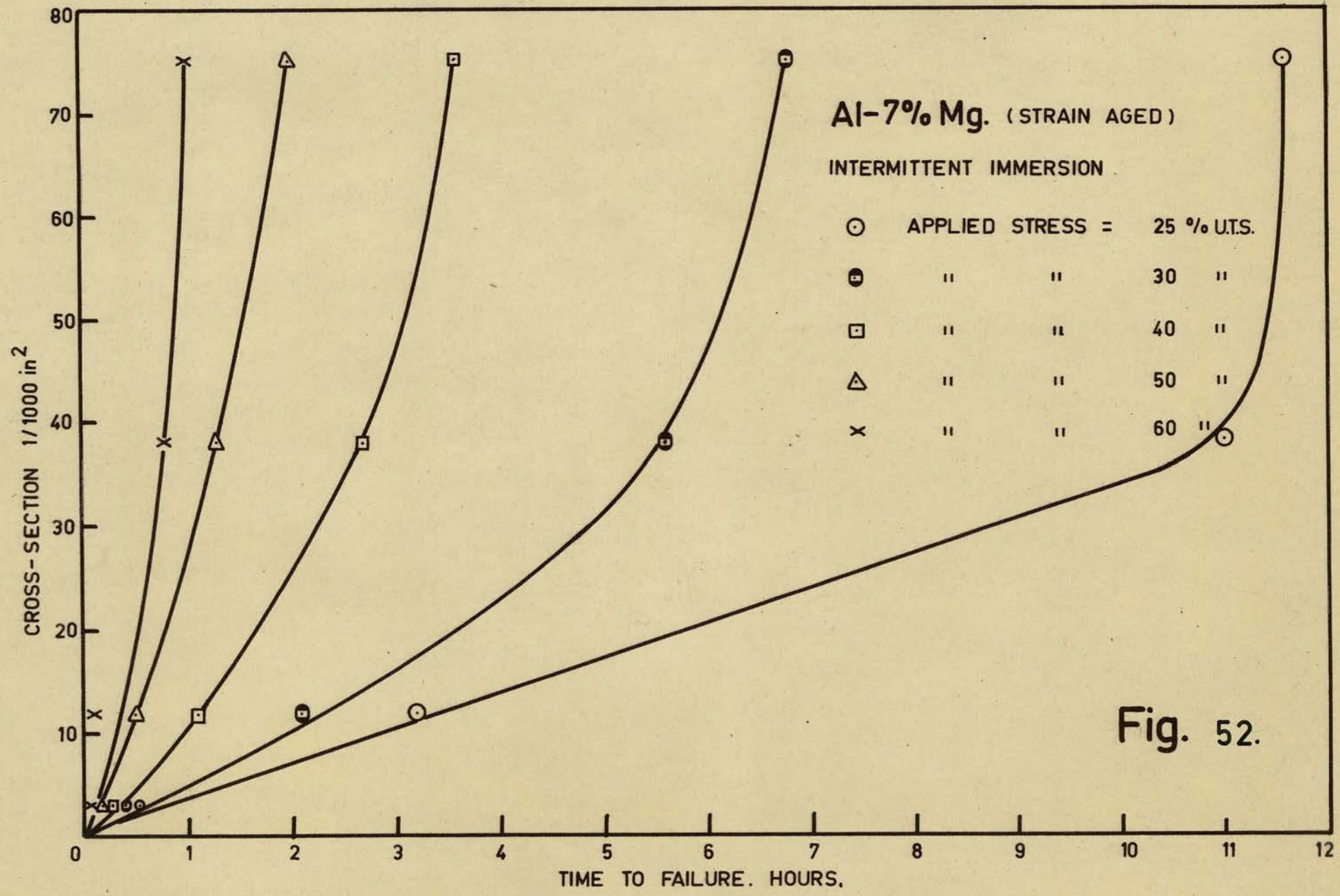

Al-7% Mg. (STRAIN AGED)
INTERMITTENT IMMERSION
APPLIED STRESS = 25 % U.T.S.
" " 30 "
" " 40 "
" " 50 "
" " 60 "
CROSS-SECTION 1/1000 in²
TIME TO FAILURE. HOURS.
0
1
2
3
4
5
6
7
8
9
10
11
12
10
20
30
40
50
60
70
80

Fig. 52.

TABLES.

TABLE 1.

Alloy	Mg.	Mn.	Fe.	Si.	Cu.
Al-2¼%Mg.	3.70	0.18	0.29	0.19	0.08
Al-3½%Mg.	2.01	0.32	0.27	0.20	0.03
Al-5%Mg.	4.8	0.28	0.20	0.15	Trace
Al-7%Mg.	6.07[x]	0.33	0.22	0.19	0.06

Analyses by James Booth & Co., Birmingham.

[x]Sample too small for precise Mg. analysis.

TABLE 2.

Alloy	0.1% Proof Stress		U.T.S.	
	lb./x.s.	Tons/in.^{2}	lb./x.s.	Tons/in.^{2}
Al-2¼%Mg.	56	8.5	82	12.8
Al-3½%Mg.	80	12.1	115	17.4
Al-5%Mg.	81	12.3	124	18.8
Al-7%Mg.	93	14.0	147	22.2

TABLE 3. (Fig. 3)

Al-3½%Mg.

Unstressed corrosion-time curve

Intermittent Immersion

Hours exposed	% Loss	U. T. S.
10	0	2.6
16	0.4	2.2
24	3.5	8.7
35	6.9	9.6
48	12.2	10.0
49	14.8	8.7
67	18.3	22.6
77	22.2	19.1
97	30.4	26.5
120	27.4	31.5
144	33.9	31.8
163	37.4	37.0
192	41.3	35.2
211	41.3	43.5
240	40.0	43.1
282	44.4	50.5
306	48.5	
335	48.7	

TABLE 4. (Fig. 2)

Al-3½%Mg.

Stressed corrosion-time curve

Intermittent Immersion

Applied stress % U.T.S.	Time to failure hours	Mean time to failure
69.6	28,30,19,24,30,45,19,41,20,(93.5)	28.5
60.9	37,43,35,30,37,39,35,34,27,30,(321)	34.7
52.2	72,110,92,97,94,136,59,66,192,237	116
43.5	343, 410	-
34.8	366, 432	-

TABLE 5. (Fig. 4)

Al-3½%Mg.

Stress-corrosion susceptibility

Intermittent Immersion

Applied stress % U.T.S.	S_u^c	S_s^c	f_s^c
70	3.5	30	26.5
65	7.5	35	27.5
60	13.5	40	26.5
55	21.5	45	23.5
52.2	29.5	47.8	18.3

TABLE 6. (Fig. 5)

Al-2¼%Mg.

Unstressed corrosion-time curve

Intermittent Immersion

Hours exposed	% Loss	U.T.S.
25	0	2.4
71	1.2	4.3
119	4.9	10.4
144	7.3	12.2
162	11.0	9.8
168	11.0	15.9
175	18.3	15.2
192	28.0	19.5
221	23.8	18.3
239	28.7	36.6
264	36.6	37.8
330	33.0	37.8

TABLE 7. (Fig. 7)

Al-2¼%Mg.

Stress-corrosion susceptibility

Intermittent Immersion

Applied stress % U.T.S.	Time to failure hours	S_u^c	S_s^c	f_s^c
67.1	345, 296, 368, 429 — Mean 360	35.0	32.9	-2.1
61.0	390*	35.0	39.0	4.0

*one result only

TABLE 8. (Fig. 6)

Mg.% vs. stress-corrosion susceptibility

Intermittent Immersion

%Mg. Nominal	%Mg. Actual	Stress-corrosion susceptibility %	Corrected susceptibilities
2 1/4	2.01	0	0
3 1/2	3.70	18.4	9.4
5	4.80	45.0 *	33.0
7	6.85	79.0 * Curve (b) Fig. 6.	71.0 Curve (a) Fig.6

* (3)

TABLE 9. (Fig. 14)

Al-3½%Mg.

Unstressed corrosion-time curve

Spray

Hours exposed	% Loss	U.T.S.
45	7.0	4.4
95	8.7	5.2
164	13.0	15.6
220	27.0	20.9
268	23.5	25.2
316	20.0	27.0

TABLE 10. (Fig. 15)

Al-3½%Mg.

Stressed corrosion-time curve

Spray

Applied Stress % U.T.S.	Time to failure hours
65.3	82, 66, 70
60.9	109, 88
56.5	142, 138
52.2	231, 336

TABLE 11. (Fig. 16)

Al-3½%Mg.

Stress-corrosion susceptibility

Spray

Applied Stress % U.T.S.	S_u^c	S_s^c	f_s^c
65	5.5	35	29.5
60	7.7	40	32.3
55	14.0	45	31.0
52.2	25.0	47.8	22.8

TABLE 12. (Fig. 17)

Al-7%Mg.

Unstressed corrosion-time curve

Spray

Hours exposed	% Loss U.T.S.
21.5	31.5, 30.9
47.3	53.5, 67.8
72.0	85.9, 93.3

TABLE 13. (Fig. 17)

Al-7%Mg.

Unstressed corrosion-time curve

Intermittent Immersion

Hours exposed	% Loss U.T.S.
21.5	55.8, 51.7
42.5	94.6, 95.3

TABLE 14. (Fig. 19)

Al-7%Mg.

Stressed corrosion-time curve

Spray

Applied Stress % U.T.S.	Time to failure Minutes
60.4	7.0, 8.0
53.7	13.0, 16.0
47.0	20, 18
40.3	29.5, 32
36.9	49, 36, 36
30.9	52, 52
24.2	52, 85, 75, 114
18.1	269, 237
10.1	1268, 1390
3.0	4020, 3270, 4380

TABLE 15. (Fig. 18)

Al-7%Mg.

Stressed corrosion-time curve

Intermittent Immersion

Applied Stress % U.T.S.	Time to failure Minutes
60.4	6, 4
53.7	4.5, 5
47.0	10.5, 10
40.3	14, 15.5
33.6	20.5, 20
26.8	32, 33
20.1	56, 60, 85
18.1	275, 265
10.1	925, 910
3.0	2085, 2760

TABLE 16. (Fig. 21)

Al-7%Mg.

Stress-corrosion susceptibility

Spray

Applied stress % U.T.S.	S_u^c	S_s^c	f_s^c
60	0.4	40	39.6
55	0.5	45	44.5
50	0.7	50	49.3
45	0.9	55	54.1
40	1.0	60	59.0
35	1.2	65	63.8
30	1.7	70	68.3
25	2.1	75	72.9
20	3.1	80	76.9
18.1	7.8	81.9	74.1
10.1	32.5	89.9	57.4
3.0	81.2	97.0	15.8

TABLE 17. (Fig. 22)

Al-7%Mg.

Stress-corrosion susceptibility

Intermittent Immersion

Applied stress % U.T.S.	S_u^c	S_s^c	f_s^c
60.0	0.2	40.0	39.8
55.0	0.3	45.0	44.7
50.0	0.4	50.0	49.6
45.0	0.6	55.0	54.4
40.0	0.8	60.0	59.2
35.0	1.0	65.0	64.0
30.0	1.3	70.0	68.7
25.0	2.1	75.0	72.9
20.0	4.0	80.0	76.0
18.1	13.5	81.9	68.4
10.1	41.0	89.9	48.9
3.0	92.0	97.0	5.0

TABLE 18. (Fig. 23)

Al-5%Mg.

Unstressed corrosion-time curve

Spray

Hours exposed	% Loss U.T.S.
24	0.8, 3.3, 3.7, 2.5
48	4.1, 3.3, 2.5, 4.1
72	7.5, 5.4, 6.6, 7.5
96	6.6, 8.3, 4.1, 5.8
120	6.6, 8.3, 5.0
144	15.7, 9.1, 8.3, 9.1
168	9.9, 14.0
191	12.4, 13.2
217	9.9, 12.4
239	17.4, 19.8

TABLE 19. (Fig. 20)

Al-3½%Mg.

Unstressed corrosion-time curve

Intermittent Immersion

Film removed every 24 hours

Hours exposed	% Loss U.T.S.	Mean % Loss U.T.S.
96	29.6, 24.4	27.0
144	40.9, 27.8, 33.1	33.9
239	47.9, 47.0	47.5
309	54.8, 55.6, 51.3	53.9

TABLE 20.

Al-7% Mg chemical analyses

S.W.G.	Mg.	Mn.	Fe.	Si.	Cu.	Ti.	Zn.
0	6.78	0.27	0.27	0.15	0.04	0.086	0.02
4	6.99	0.29	0.28	0.16	0.04	0.094	0.02
8	6.73	0.29	0.30	0.15	0.04	0.096	0.02
10	6.91	0.26	0.26	0.16	0.04	0.090	0.02
16	6.14*	0.33	0.19	0.27	0.11	0.086	0.02

Analyses by James Booth & Co., Birmingham.

*Sample too small for precise Mg. analysis.

TABLE 21.

Al-7%Mg. Gauge 0, 4, 8, 10, 16

Average mechanical properties.

Gauge	X.S. $in.^2$	U.T.S. lb./x.s.	U.T.S. $Tons/in.^2$	0.1% P.S. lb./x.s.	0.1% P.S. $Tons/in.^2$
0	0.07510	4120	25.4	2595	15.4
4	0.03800	2120	24.9	1323	15.8
8	0.01838	1000	24.3	620	15.1
10	0.01168	634	24.2	370	14.2
16	0.00296	147	22.2	93	14.0

TABLE 22. (Fig. 29)

Al-7%Mg. Gauge 0

Unstressed corrosion-time curve

Intermittent Immersion

Hours exposed	% Loss U.T.S.
23.5	23.8, 19.9
48.0	37.4, 36.0
71.3	45.9 47.4
95.3	54.2, 54.3
118.5	60.8, 62.4
215.0	87.0, 86.4
166.3	75.6, 74.3
187.3	79.3, 84.0
230.0	86.0, 87.0

TABLE 23. (Fig. 30)

Al-7%Mg. Gauge 4

Unstressed corrosion-time curve

Intermittent Immersion

Hours exposed	% Loss U.T.S.
25.5	27.8, 27.8
50.0	43.6, 45.6
72.3	61.0, 58.0
96.5	66.0, 65.7
120.0	81.3, 78.8
166.8	84.9, 82.5

TABLE 24. (Fig. 31)

Al-7%Mg. Gauge 8

Unstressed corrosion-time curve

Intermittent Immersion

Hours exposed	% Loss U.T.S.
24.0	33.9, 35.5, 34.0, 42.0
48.7	44.0, 47.8, 57.2
75.0	64.5, 80.4
123.0	86.0, 82.0
143.0	83.5, 84.1
166.0	87.6, 84.9
72.0	68.0, 80.0
96.0	83.3, 84.2
113.0	90.7
163.0	87.1, 85.5

TABLE 25. (Fig. 33)

Al-7%Mg. Gauge 10

Unstressed corrosion-time curve

Intermittent Immersion

Hours exposed	% Loss U.T.S.
26.0	40.4, 40.2
47.0	66.9, 64.2
68.0	81.4, 84.0
70.3	83.0
113.3	93.7, 95.3

TABLE 26. (Fig. 35)

Al-7%Mg. Gauge 16

Unstressed corrosion-time curve

Intermittent Immersion

Hours exposed	% Loss U.T.S.
21.5	55.8, 51.7
42.5	94.6, 95.3

TABLE 27. (Fig. 37)

Al-7%Mg. Gauge 0

Stressed corrosion-time curve

Intermittent Immersion

Applied Stress % U.T.S.	Time to failure hours
61.5	0.9, 1.1
54.6	1.5, 1.5
47.8	2.9, 2.6
40.4	4.7, 3.0, 4.1
33.7	4.2, 4.8
30.3	7.9, 6.0
23.6	16.3, 18.2
20.5	38.0, 31.0
13.7	62.5, 67.8

TABLE 28. (Fig. 38)

Al.-7%Mg. Gauge 4

Stressed corrosion-time curve

Intermittent Immersion

Applied Stress % U.T.S.	Time to failure hours
57.5	0.6, 0.9, 0.9
53.1	1.1, 1.1
45.8	1.7, 1.7
39.8	2.3, 3.3, 3.2
32.7	4.6, 3.9
28.1	6.9, 7.3
22.4	26.0, 25.8
16.8	58.8, 75.2

TABLE 29. (Fig. 32)

Al-7%Mg. Gauge 8

Stressed corrosion-time curve

Intermittent Immersion

Applied Stress % U.T.S.	Time to failure hours
59.5	0.5, 0.7
47.6	1.3, 1.3
39.7	2.3, 2.7
31.7	6.5, 5.8
26.5	10.5, 14.2
19.8	32.2, 39.3

TABLE 30. (Fig. 34)

Al-7%Mg. Gauge 10

Stressed corrosion-time curve

Intermittent Immersion

Applied Stress % U.T.S.	Time to failure hours
50.0	0.6, 0.6
41.8	1.0, 0.9
31.3	1.9, 1.9
25.1	3.0, 3.3
20.8	9.4, 8.9, 8.8
12.4	28.2, 33.1

TABLE 31. (Fig. 36)

Al-7%Mg. Gauge 16

Stressed corrosion-time curve

Intermittent Immersion

Applied Stress % U.T.S.	Time to failure	
	Min.	Hours
54.5	6.0, 8.0	0.10, 0.13
47.6	11.0, 12.0	0.18, 0.20
40.8	13.0, 15.0	0.22, 0.25
27.2	27.0, 28.0	0.45, 0.47
18.4	200,212,247	3.3,3.5,4.1

TABLE 32. (Fig. 39)

Al-7%Mg. Gauge O

Stress-corrosion susceptibility

Intermittent Immersion

Applied Stress % U.T.S.	S_u^c	S_s^c	f_s^c
60.0	1.0	40.0	39.0
50.0	2.5	50.0	47.5
40.0	4.0	60.0	56.0
30.0	8.0	70.0	62.0
25.0	12.5	75.0	62.5
22.0	21.0	78.0	57.0
20.5	29.0	79.5	50.5
13.7	44.0	86.3	42.3

TABLE 33. (Fig. 40)

Al-7%Mg. Gauge 4

Stress-corrosion susceptibility

Intermittent Immersion

Applied Stress % U.T.S.	S_u^c	S_s^c	f_s^c
60.0	1.0	40.0	39.0
55.0	1.5	45.0	43.5
50.0	2.0	50.0	48.0
45.0	3.0	55.0	52.0
40.0	4.0	60.0	54.0
35.0	5.0	65.0	60.0
30.0	7.5	70.0	62.5
25.0	14.0	75.0	61.0
20.0	39.0	80.0	41.0
16.8	56.0	83.2	27.2

TABLE 34. (Fig. 41)

Al-7%Mg. Gauge 8

Stress-corrosion susceptibility

Intermittent Immersion

Applied Stress % U.T.S.	S_u^c	S_s^c	f_s^c
60.0	1.5	40.0	38.5
50.0	3.0	50.0	47.0
40.0	6.5	60.0	53.5
35.0	9.0	65.0	55.0
30.0	14.5	70.0	54.0
25.0	25.5	75.0	49.5
22.5	35.0	77.5	42.5
20.0	46.5	80.0	36.0

TABLE 35. (Fig. 42)

Al-7%Mg. Gauge 10

Stress-corrosion susceptibility

Intermittent Immersion

Applied Stress % U.T.S.	S_u^c	S_s^c	f_s^c
60	0	40.0	40.0
50	1.0	50.0	49.0
40	2.0	60.0	58.0
30	4.0	70.0	66.0
25	6.0	75.0	69.0
20	17.5	80.0	62.5
15	36.0	85.0	49.0
10	54.0	90.0	36.0

TABLE 36. (Fig. 43)

Al-7%Mg. Gauge 16

Stress-corrosion susceptibility

Intermittent Immersion

Applied Stress % U.T.S.	S_u^c	S_s^c	f_s^c
60.0	0.2	40.0	39.8
50.0	0.4	50.0	49.6
40.0	0.6	60.0	59.4
30.0	1.0	70.0	69.0
25.0	1.3	75.0	73.7
20.0	2.4	80.0	77.6
18.4	8.0	81.6	73.6

TABLE 37. (Fig. 44)

Al-7% Mg.

Slope of unstressed corrosion-time curve vs. cross-section

Nominal Gauge B.S.W.G.	Cross-section square inches	Slope of U.S. curve x 10		
		0-20 hours	0-40 hours	0-60 hours
0	0.075	9.75	8.00	6.91
4	0.038	11.50	9.50	8.50
8	0.018	15.75	12.75	11.08
10	0.012	16.00	14.25	13.00
16	0.003	25.00	22.50	-*

* The curve of gauge 16 can reasonably be extrapolated to 100% loss of U.T.S. at less than 60 hours.

TABLE 38.

Al-7%Mg. Gauge 0, 4, 8, 10 and 16.

Depth of penetration of corrosion at T hours.

Gauge	x Diameter inches	Radial depth of annulus of corrosion. Inches			
		T = 25	T = 50	T = 100	T=150
0	0.309	0.019	0.032	0.052	0.070
4	0.220	0.016	0.028	0.050	0.075
8	0.153	0.016	0.026	-	-
10	0.122	0.013	0.027	-	-
16	0.061	0.012	-	-	-

x i.e. after strain-ageing.

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